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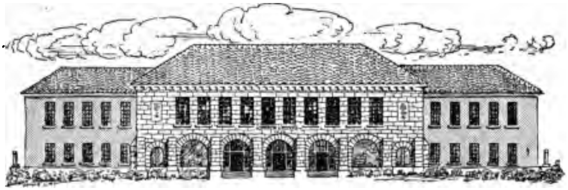

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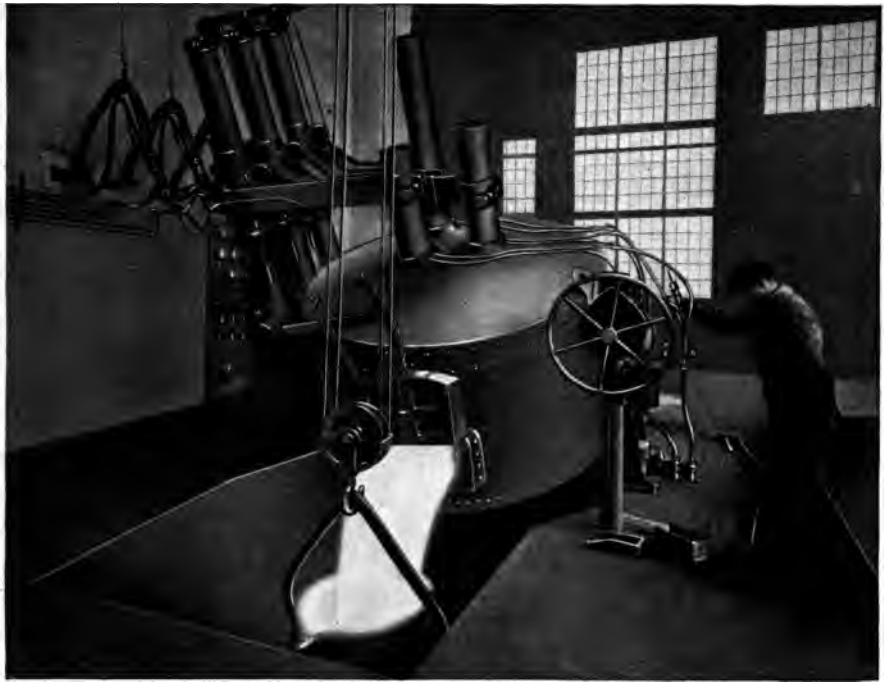

POURING MOLTEN STEEL FROM AN ELECTRIC FURNACE

PRACTICAL CHEMISTRY

FUNDAMENTAL FACTS AND APPLICATIONS TO MODERN LIFE

BY

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New York
THE MACMILLAN COMPANY
1920

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Set up and electrotyped. Published May, 1920.

Norwood Press
J. S. Cushing Co. — Berwick & Smith Co.
Norwood, Mass., U.S.A.

PREFACE

CHEMISTRY is so closely connected with many phases of modern life that almost everyone should have some knowledge of it. Its application to the problems of industry and recently to those of warfare has attracted unusual attention and interest. It plays no less important a part in the sciences of agriculture and medicine. For these reasons we believe that a knowledge of the *fundamental facts of chemistry* and an ability to use them should form a part of the equipment of our American youth.

It is generally conceded that in order to teach any subject effectively it is first necessary to arouse an interest in it. Fortunately this is an easy task in chemistry if the method of presenting the subject is not too formal and academic. We have found two ways of awakening the student's interest: first, by appealing to his love of the miraculous and dramatic; and second, by touching his curiosity concerning the things of every-day life. With this in view, we have outlined *numerous class-experiments to be done on the lecture-table*, often somewhat spectacular; and, wherever possible, we have drawn examples of *chemical phenomena from the student's daily experience.* Such applications of the facts and principles of chemistry, we believe, make the subject real and practical. A young person is not interested in the details of large manufacturing operations which he may never see, but he is curious concerning the composition and transformation of many familiar products.

It is important that the economic significance of chemistry and the allied industries be realized. To this end the idea has gradually been developed throughout the book that some of the common chemical materials, such as sulfuric acid, soda, and steel, *are literally* foundation stones of modern civilization.

The Industrial Chart (p. 205) helps to fix in the student's mind the coördination of a number of chemical industries.

The chemistry of the carbon compounds has been treated in a very elementary way but at some length because so many organic substances are familiar and important. The chemistry of growing things, including the subject of fertilizers, has been considered in several places because of the importance of agriculture.

In selecting the material for this book we have tried to include only those topics which young people can readily grasp and will find useful in their every-day life. In doing this we have covered the topics suggested by the College Entrance Examination Board for admission to colleges and scientific schools. We have intentionally included somewhat more material than it is probably advisable for any class to undertake in a single year. This enables the teacher to vary his work from year to year and to adapt his instruction to the ability and needs of his class. Some teachers may prefer to use the chapter on gases and their measurement (V) as collateral reading in connection with the laboratory work; and some may be inclined to postpone the chapter on atomic and molecular weights (XIII) until more facts have been studied. The chapters on chemical equilibrium (XXI), on hypochlorous acid (XXVII), on some of the less common elements (XXXV), and on radioactivity (XXXVI) may be omitted without breaking the continuity of the subject.

Our observation of the results of the first year's course in chemistry leads us to urge teachers not to try to cover too much ground, but to select carefully just what material they can best use and to teach that *thoroughly*. Many a student is lost in a maze of chemical theories before he reaches the important chemical facts which he can use. We have tried to introduce theories when and in so far as they would help the student to understand the essential facts of chemistry. In order to focus attention on what we consider these fundamentals, we have placed at the end of each chapter a *summary*, so worded as to be easily remembered and applied.

It is hoped that some students will want to continue their study of chemistry either at school or at home. To stimulate and perhaps to guide these efforts at independent work, we have suggested at frequent intervals in the book some suitable *topics for further study*, together with some leading questions.

We are greatly indebted to many of our friends who have assisted in the preparation of this book: especially to Professor Elmer P. Kohler, who has read the entire manuscript and made many valuable suggestions; to Professor Theodore W. Richards, who lent us from his own collection portraits of famous chemists; and to Dr. Norris F. Hall, who has read certain chapters. We have made an especial effort to prepare a *text that will not only be clear but readily understandable*, and in this we have been greatly assisted by Dr. D. O. S. Lowell, Headmaster of the Roxbury Latin School. A large share of the credit for such success as we have achieved in illustrating the book is due to the deftness and patience of Mr. James S. Conant of the Suffolk Engraving and Electrotyping Co.

N. H. B.
J. B. C.

Note. — The directions for laboratory experiments to accompany the study of this book are printed in a separate volume.

ACKNOWLEDGMENT

We are greatly indebted to many people for assistance in securing suitable illustrations and especially to the following:

Dr. Charles W. Eliot, Cambridge (243); Mr. Charles R. Gow, Boston (219); Mr. Frederick G. Keyes, Mass. Institute of Technology (189); Mr. C. Neimeyer, Duluth (234); Professor Charles Palache, Department of Mineralogy at Harvard (88); Mr. Harry S. Thatcher, Los Angeles (169).

We are also very glad to acknowledge the courtesy of many institutions and concerns in furnishing reliable data and illustrations. We would especially mention here the following:

Frank G. Allen, Houston (151); Acheson Graphite Co., Niagara Falls (144); Air Reduction Co., N. Y. (64); American Engineering Co., Philadelphia (150); The Barrett Co., N. Y. (153); Bethlehem Steel Co., Bethlehem (161, 221, 223, 227, 230, 231); Carnegie Steel Co., Pittsburgh (228); Chemical Laboratory of Harvard College (204, 245); Colorado Iron Works Co., Denver (244); Continental Salt & Chemical Co., San Francisco (177); Emerson Apparatus Co., Boston (149); Ford Motor Co., Detroit (5); General Electric Co., Schenectady (147); Goodyear Tire & Rubber Co., Akron (112); Grinnell Automatic Sprinkler, Providence (202); The Walter E. Lummus Co., Boston (164); Bureau of Mines, Pittsburgh (60); Pittsburgh Furnace Co., Milwaukee (Frontispiece); The Permutit Co., N. Y. (215–16); C. C. Pierce & Co., Los Angeles (90); The Radium Company of Colorado, Denver (250); Raritan Copper Works, Perth Amboy (239); Standard Oil Co., N. Y. (152); The Solvay Process Co., Syracuse (180); Metal & Thermit Corporation, N. Y. (210); The Union Sulfur Co., N. Y. (105); Vulcan Iron Works, Wilkes-Barre (218); Wallace & Tiernan Co., N. Y. (197); The Warner Chemical Co., N. Y. (178–9).

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PRACTICAL CHEMISTRY

PRACTICAL CHEMISTRY

CHAPTER I

CHEMICAL CHANGE

Chemical changes in everyday life — what chemistry is about — what happens in a chemical change — how we recognize materials — characteristics of a chemical change — no change of weight in a chemical process — what is the work of a chemist?

1. Chemical changes in everyday life. Everyone is familiar with the fact that when wood burns a great deal of heat is produced and, except for a few particles of ashes, the original wood entirely disappears. This is such a common occurrence that we do not generally appreciate its striking significance. Apparently there has been some sort of change during the burning, for we can now no longer find any of the original wood. Another change almost as striking occurs if we allow a piece of iron, such as a rail, to lie for some time exposed to the weather. We find that it first becomes coated and then crumbles to a mass of brown powder which we call rust. In these cases such well-known substances as wood and iron have disappeared before our very eyes. These profound changes are examples of natural processes which are known as **chemical changes**. The decay of wood, the souring of milk, the putrefaction of meat are likewise common examples of chemical change; still others are the explosion of gasolene in an automobile cylinder, the sudden burning of a flash-light powder, and the *bursting of a high*-explosive shell. In all these cases certain materials disappear and new ones are formed; in every instance the properties of the product of the change are plainly different from those of the original materials.

2. What is chemistry about? The changes of which we have just spoken are so important to everyday life and are apparently so fundamental that a whole branch of science is devoted to their study. Chemistry considers just such changes as those involved in the burning of wood and the souring of milk. To one trained in this science these apparently mysterious transformations seem relatively simple. A chemist is able to predict whether a given substance will burn or not. He can also tell us what happens when milk sours and how to prevent it. Similarly chemists have been able to devise methods for preventing the rusting of iron. With the aid of chemistry it has been possible to manufacture a great number of useful materials, such as dyes, medicines, and explosives. Dynamite, for instance, is a material which under certain conditions undergoes a rapid change and produces a tremendous amount of force.

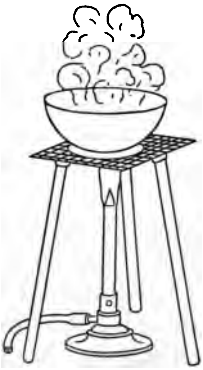

Fig. 1. Action of nitric acid on iron.

All the changes which occur in living matter, both plants and animals, are chemical changes. All the food that we eat goes through a number of complicated changes in our body. All processes of cooking involve chemical changes which, for the most part, render food more palatable and easier to digest. For example, the white of an egg, a thick colorless liquid, is turned by boiling into a soft white solid. It is evident that chemistry is the foundation of the sciences of biology and medicine.

3. What happens in a chemical change? Let us now see *just what* happens in some cases of chemical change.

Suppose we drop a few small iron nails into a liquid called nitric acid (Fig. 1). We notice that the iron dissolves rapidly and that a cloud of brown fumes is produced. When we evaporate the solution over a flame, we find that a brown solid is left behind (Fig. 1). We can clearly see that this is not the iron with which we started. It is a new material quite different from iron.

In every chemical change one or more materials disappear and one or more new substances are formed.

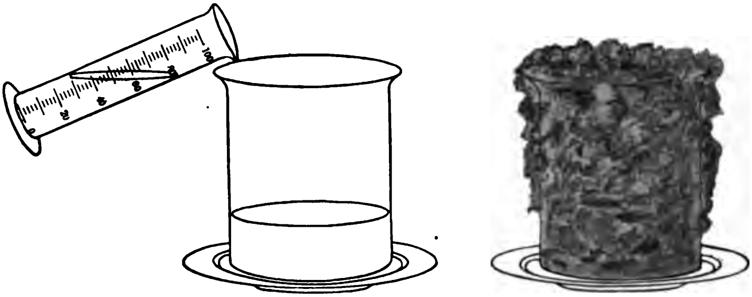

Fig. 2. Charring of sugar by sulfuric acid.

If we put a solution of sugar into a glass and pour on it a little concentrated sulfuric acid, we see a remarkable transformation (Fig. 2). A mass of black froth immediately appears in place of the sugar, and if we examine the black solid in this froth we shall look in vain for our original sugar.

A little finely ground sulfur and zinc dust may be mixed together and put in a small pile. When this mixture is touched with a flame a flash at once appears and a cloud of white solid floats off. Again we find neither our original sulfur nor zinc, but only a new white substance, which in this case is known as zinc sulfide.

In this last experiment not only was a new material formed but there was considerable heat and light produced. We usually find **that in a chemical change heat is either absorbed or evolved and light is often emitted.**

4. How we recognize materials. When we notice that ashes are different from wood and that the brown solid formed by dissolving nails in nitric acid is different from metallic iron, we are unconsciously taking advantage of our everyday knowledge of what such common materials as wood and iron are really like. No one would have any difficulty in distinguishing between a stick of wood and a bar of iron, even if the stick were painted black. Wood will float readily on water, iron will not. A magnet will attract a piece of iron and not a piece of wood. Wood easily catches fire whereas iron will not burn. Such characteristic facts about a given material are called its **properties**. We can recognize and identify any particular material by knowing a number of these properties.

Many properties of materials can be determined accurately and expressed by numbers. For example, the weight of a unit volume of matter is called the **density** and is expressed *in grams per cubic centimeter*. Iron, which is heavy, has a density of about 7; pine wood, being light, has a density of about 0.4. By determining such properties accurately we have a quick and convenient method of identifying various materials. Usually, however, it is necessary to determine several properties in order to be sure that we have completely identified the material. Other useful properties are solubility, color, melting point, and boiling point.

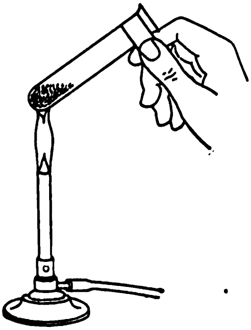

Fig. 3. Heating iron powder and sulfur.

5. Characteristics of a chemical change. Let us take some finely divided sulfur and some iron filings. We notice that the sulfur is a yellow powder, relatively light; it will dissolve in a liquid called carbon disulfide. The iron is a heavy gray solid, insoluble in carbon disulfide, and readily attracted by a magnet. Let us mix these two materials together in such proportions that there is about twice as much sulfur (by volume) as iron. We place the mixture in a test tube and heat it in a flame (Fig. 3). It will be seen that in a few moments a glow spreads all through the contents of the tube, and this glow continues for a time even when the flame is removed. Evidently something has happened in the tube which has produced heat and light. If we break the test tube and examine the solid, we shall see that it is a hard black mass. If we grind it up into small bits we shall find that *none of it has the properties either of sulfur or of iron.* That is, none of it is soluble in carbon disulfide, and none of it is attracted by a magnet.

In this experiment the two substances, iron and sulfur, have disappeared and a new substance which is called iron sulfide has been formed. We are able to recognize these facts by carefully noting the properties of the original materials and the properties of the final product. *In a chemical change there is always a change in the properties of the materials involved.*

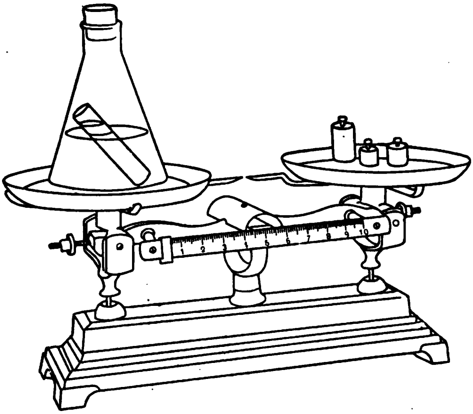

Fig. 4. Chemical change in a closed vessel; no change in weight.

6. No change in weight in a chemical process. If we had carefully weighed the test tube containing the iron and sulfur before and after heating, we should have found that *no change in weight had taken place.* This is such a general and important fact in chemistry that we may very well illustrate it by another experiment.

We may select any two substances which act quickly on one another when brought together. For example, suppose we take silver nitrate and caustic potash solutions and pour one into a short test tube and the other into a flask. We place the tube in the flask, as shown in figure 4, carefully close it, and determine its weight. Then we tilt the flask so as to bring the two clear liquids together, and we produce a brown-black substance. The chemical change causes some rise in temperature. After the flask has cooled we again weigh it and find that *its weight is unchanged.*

A large number of such experiments have been performed with great precision, and these have shown that *in every chemical change the weight of the materials taking part in the change is exactly equal to the weight of the substances produced by the change.* This is known as the LAW OF CONSERVATION OF MATTER.

A **law** in science is simply a statement of some general fact which has been established by a large number of experiments. It is a description of the constant mode of behavior of certain materials under certain conditions.

Fig. 5. Chemical laboratory in Ford Motor plant; steel and other materials used in the manufacture are tested here.

7. What is the work of a chemist? We have seen that chemistry deals with such widely different processes as the explosion of gunpowder and the digestion of food. Consequently a chemist's work covers a broad field. Almost all manufacturing operations involve one or more chemical processes. Manufacturers, therefore, have to employ chemists

(Fig. 5) to see that these are carried out satisfactorily; in the same plant other chemists are often engaged in trying to improve the manufacturing methods. Oftentimes the chemist is able to find some way in which to turn a waste product of the industry into some useful and valuable material.

Soap, fertilizers, glass, paper, and ink are common materials which are made by a series of rather complicated chemical changes. Their manufacture has been much improved by the work of chemists. Explosives, dyes, and many drugs were first made in the chemical laboratory, were found to be valuable, and were then produced on a large scale.

The chemist is also often employed to find out of what various things are made. For example, he determines whether there is any zinc, copper, or gold in a given rock and how much of each metal. He detects poison in food and drink; he measures the amount of sugar in a given beet or the amount of valuable material in a fertilizer. Medical and biological work carried out in hospitals and special laboratories requires the assistance of many chemists.

SUMMARY OF CHAPTER I

CHEMICAL CHANGE involves a change in the identity of the material; *all* the characteristic properties disappear; one or more new materials are formed.

THE PROPERTIES of a material are the characteristics by which we identify it, such as its color, hardness, taste, density, solubility, and melting point.

HEAT and light often attend a chemical change.

LAW OF CONSERVATION OF MATTER. The weight of the materials taking part in a chemical change is exactly equal to the weight of the materials produced by the change.

CHEMISTRY deals with the composition of materials and with the changes which they may undergo. The chemist is often able to improve methods of manufacture and to find new uses for *waste products.*

QUESTIONS

1. If sand and sugar are mixed together, what property of each would you use in separating them?

2. What properties would you make use of in distinguishing between (*a*) copper wire and iron wire, (*b*) wood and iron, (*c*) aluminum and silver, and (*d*) powdered sugar and flour?

3. Name five examples of chemical change (not mentioned in the text) with which you are familiar.

4. If we pound iron it becomes hot. Have we produced a chemical change?

5. If we scratch a match on a box we produce both heat and light. Is this a chemical change? Give your reasons.

6. Name some property which is common to all materials.

7. Show how the Law of Conservation of Matter applies to the chemical change involved in burning coal in a stove.

8. In what ways did chemistry play an important part in the World War?

9. Why is chemistry of such great value in agriculture?

10. How does the government make use of the chemist in the enforcement of "pure food" laws?

CHAPTER II

ELEMENTS AND COMPOUNDS

Substances and mixtures — compounds — elements — compounds made from elements — compounds have a definite composition — mixtures and compounds compared — separation of mixtures — occurrence of the elements — number and importance of compounds.

8. Substances and mixtures. In the first chapter we learned that any material could be recognized by its characteristic properties. If we examine with a magnifying glass a bit of soil from the garden (Fig. 6), we shall probably find that it is composed of at least two differently colored particles, — one, a white glassy material, which is sand, and the other, brownish dirt composed of clay mixed with the remains of plants that have decayed. If we rub the soil between our fingers we find that the bits of sand are hard and sharp while the clayey material is soft and easily crumbles. In this way we learn that ordinary garden soil is composed of two or more materials which have entirely different properties. Material such as soil is obviously a mixture.

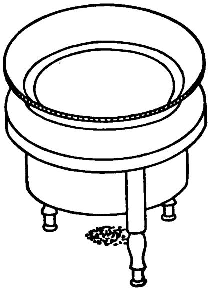

Fig. 6. Soil examined under a magnifying glass.

If we examine the mixture of iron and sulfur which we used in the last chapter, we can recognize in it particles of sulfur and particles of iron. On the other hand, if we examine a mass of iron filings or a pile of powdered sulfur, we find that every particle is like *every other* particle and seems to have exactly the same properties. *A material of which every part is like every other part is said to be homogeneous* and is called by the chemist a **substance.** A material which is composed of two or more substances mixed up together is called a **mixture.** The soil is therefore a mixture and not a substance. Sulfur and iron are substances which we can easily stir together to form various mixtures.

Since a substance is a homogeneous material, all parts of it will have exactly the same properties. Every sample of the substance will be found to be exactly like every other sample. On the other hand, the properties of a mixture will depend on how much of each component is present. For example, a mixture of 10 parts of iron and 1 part of sulfur is gray, while a mixture of 10 parts of sulfur and 1 of iron is almost pure yellow.

Therefore, if we find that all specimens of a material have exactly the same properties, we may feel certain that we are dealing with a substance and not a mixture.

9. Chemical compounds. Probably the most important as well as the most familiar substance is water. Yet, strange as it may seem, even pure water is not a simple substance. We may easily decompose water by an electric current into two very different substances.

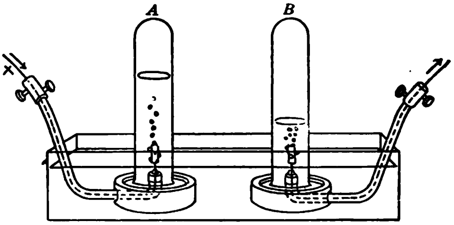

Fig. 7. Water decomposed by an electric current into oxygen and hydrogen.

We pour some water (containing a little sodium sulfate) into the apparatus shown in figure 7. The platinum electrodes are connected with a battery or generator giving at least 5 or 6 volts. The electrode in tube *A*, which is connected to the positive (+) pole, is called the **anode**, and the other electrode in *B* is the **cathode**. The current passes through the solution from the anode *A* to the cathode *B*. Small bubbles of gas are seen to rise from both electrodes, and the gas collects in *B* twice as fast as in *A*. When *B* is full we open the switch and test the collected gases. To test the gas in tube *B* we invert the tube and carefully apply a lighted match. This gas burns with a pale blue flame and is called **hydrogen.** If we invert the other tube and bring a glowing pine stick near, it bursts into a flame. This gas is **oxygen.** The sodium sulfate, which was added to make the water a better conductor of electricity, is left behind in the apparatus undiminished.

Thus we see that water is decomposed by electricity into its constituent elements, hydrogen and oxygen. This process of decomposing a compound by means of an electric current is called *electrolysis.*

Let us examine a red powder called **red oxide of mercury.** It is apparently a definite substance; every particle seems to be like every other particle.

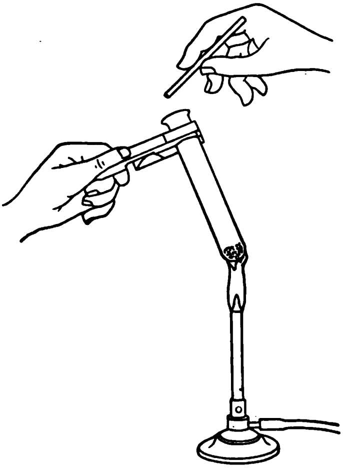

Fig. 8. Red oxide of mercury decomposed by heat.

We place some in a hard-glass test tube and arrange it for heating as shown in figure 8. Very soon the red powder becomes dark, and if we introduce into the tube a splinter of wood with a glowing spark on the end, the spark at once bursts into flame. This indicates that some gas, not air, is being evolved. On again examining the tube we notice that a part or all of the red powder has disappeared and that little drops of mercury (quicksilver) have collected on the sides of the tube. This forms a sort of mirror on the cooler part of the tube. If the heating is continued long enough all the red powder eventually disappears and is converted into two products, — **mercury,** the silvery liquid which is used in thermometers, and a gas which is called **oxygen.**

Thus, by means of heat we have transformed a definite substance, red oxide of mercury, into two other substances, mercury and oxygen. *Any substance which can be transformed* *into two or more other substances is called a* ***chemical compound.*** Hence water and red oxide of mercury are compounds.

10. What is an element? If we continue our experiments and try to produce still other substances by heating mercury, or in some other way try to decompose it, we do not succeed. Similarly, hydrogen and oxygen have never been broken down into other substances. We call such *substances which have not yet been decomposed into simpler substances* ***elements.*** There are about 85 elements (list facing back cover) from which all chemical compounds are made.

It is very remarkable to find that water is composed of two gases, one of which burns and the other makes things burn much faster than air; also, that red mercury oxide is composed of a heavy silvery liquid and a colorless gas. We see that the properties of a compound are in no way like the properties of the elements of which it is made.

11. Compounds from elements. We shall now consider the production of a compound from two elements, the reverse of the process just discussed.

We place a small quantity of iodine in a mortar and pour in a little mercury. The two substances at first remain side by side unchanged; but when we rub the mixture vigorously with a pestle (Fig. 9), a red substance, quite unlike the mercury and the iodine, is formed. This is a new substance, a compound called mercury iodide.

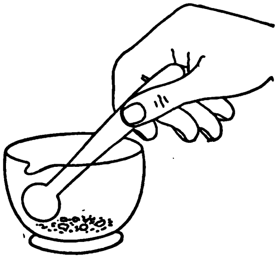

Fig. 9. Grinding mercury and iodine together in a mortar.

We are all familiar with metallic copper, which has a characteristic reddish brown color, and with sulfur, which is a brittle yellow element. If we put some copper chips and powdered sulfur into a small flask (Fig. 10) and heat it, the mixture begins to glow. The two elements unite with the evolution of heat and light. If we break the flask we find a black brittle mass which resembles neither copper nor sulfur. *The copper and sulfur have united to form a compound, copper sulfide.*

Common salt is a compound composed of two elements, — sodium, a bright, silvery, soft metal, and chlorine, a greenish yellow, poisonous gas. Sugar is a compound of carbon — an element with which we are familiar as charcoal — and two gases: hydrogen, which burns vigorously; and oxygen, which makes things burn furiously. In every case we find the same surprising difference between the properties of a compound and the properties of the elements of which it is composed.

12. Compounds have a definite composition. We shall find it convenient to represent chemical changes, or **reactions**, as they are often called, in a condensed form, thus:

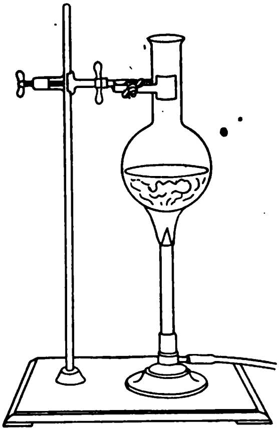

Fig. 10. Copper and sulfur heated in a flask.

$$\underset{(108)}{\text{mercury oxide}} \longrightarrow \underset{(100)}{\text{mercury}} + \underset{(8)}{\text{oxygen}}$$

In this *word equation* the arrow ($\longrightarrow$) is read *yield(s)*, and the plus sign (+) is read *and.* The numbers in parenthesis indicate the proportions by weight. Thus, it is found that 108 grams of mercury oxide yield 100 grams of mercury and 8 grams of oxygen.

Whatever quantity of mercury oxide is decomposed, experiments show that $\frac{100}{108}$ or 92.6 per cent of the weight used is left as mercury and $\frac{8}{108}$ or 7.4 per cent of the weight is oxygen.

We may represent the union of copper and sulfur to form copper sulfide thus:

$$\underset{(63.6)}{\text{copper}} + \underset{(32)}{\text{sulfur}} \longrightarrow \underset{(95.6)}{\text{copper sulfide}}$$

This means that 63.6 parts by weight of copper unite with 32 parts of sulfur to form 95.6 parts of copper sulfide.

In other words, the composition of copper sulfide is $\frac{63.6}{95.6}$ or 66.5 per cent copper and $\frac{32}{95.6}$ or 33.5 per cent sulfur.

Very careful quantitative experiments show that *every pure compound has a definite composition by weight.* The whole science of chemistry is based on this fundamental fact, which is known as the Law of Definite Proportions.

13. Mixtures and compounds. The chief difference between a mixture and a compound lies in the fact that a compound has a definite composition while in a mixture the components may be in any proportion. In water, starch, sugar, and salt we have examples of compounds, each of which has a definite composition. In flour, baking powder, and the soil we have examples of mixtures, which vary in composition.

We must also remember another difference between a mixture such as that of iron and sulfur and a compound like iron sulfide. In the mixture we can recognize the properties of both iron and sulfur and we find that the material is not homogeneous. In the compound iron sulfide, which we find to be homogeneous, we have an entirely different set of properties from those either of iron or of sulfur.

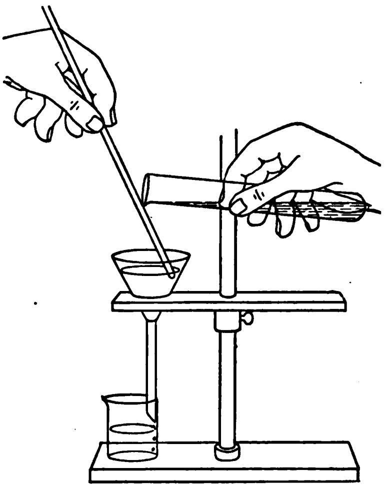

Fig. 11. Separation of iron from sulfur in solution.

14. Separation of mixtures. A mixture can often be easily separated into its ingredients. For example, the iron can be attracted away from the sulfur with a magnet; the sulfur can be dissolved away from the iron in carbon disulfide, leaving the latter behind (Fig. 11). No such simple treatment as this will separate the compound iron sulfide into iron and sulfur. As a rule we can decompose a compound into its elements only by some such drastic method as heating to a very high temperature, or passing an electric current through it.

In the mixture of iron and sulfur the particles are merely lying side by side. In the compound the elements are held together in chemical combination; and the result is that we have a substance entirely different from either of the original two elements.

15. Occurrence of the elements. Although there are some 85 elements known, only about 25 of these are at all common and important. Indeed, the accompanying diagram (Fig. 12) shows that about 98 per cent of the earth's crust, including the atmosphere, is composed of only eight elements.

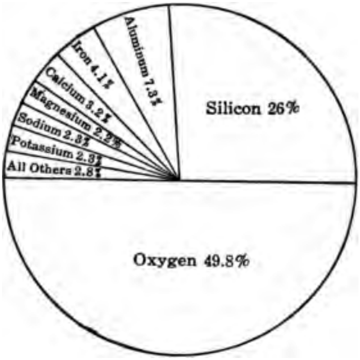

Fig. 12. Diagram showing approximately the composition of the earth's crust including the atmosphere.

Most of the elements in the earth's crust occur in combination with other elements, that is, as compounds. Occasionally some elements are found uncombined, or, as it is sometimes called, in the **free** or **native state**. Copper, sulfur, and gold may be mentioned as examples of elements which are found in the native state.

The number of elements that occur in the human body is small, and more than half of these are present in very inconsiderable amounts. The elements which are generally thought of as being essential to living plants or animals are oxygen, carbon, hydrogen, nitrogen, calcium, phosphorus, and potassium. The chemical changes which take place in living organisms are, however, very complex, and perhaps some of the other elements which occur in small quantities are equally essential.

16. Number and importance of compounds. As might be imagined, the number of compounds that can be produced by combining these eighty odd elements in different ways is very large. More than half a million are known, and new ones are being prepared and studied every day. Very fortunately only relatively few of these compounds are of importance, and therefore the study of chemistry is not so colossal a task as it otherwise would be. Moreover, as we shall see, the compounds can be divided into classes, and within these classes they are much alike. If a thorough knowledge of even a comparatively small number of compounds is obtained, the student will have a firm grasp on the fundamentals of the science.

SUMMARY OF CHAPTER II

A SUBSTANCE is homogeneous, that is, all parts are alike and show the same properties.

A MIXTURE is composed of two or more substances mixed up together.

A COMPOUND is a substance which can be decomposed into two or more substances.

AN ELEMENT is a substance which has not yet been decomposed into other substances.

LAW OF DEFINITE PROPORTIONS: Every compound has a definite composition by weight.

COMPARISON

COMPOUNDS	MIXTURES
Definite composition. **In preparation, heat or light emitted or absorbed.** **Can be decomposed only by chemical means.**	**Components in any proportion.** **In preparation, no evidence of light or heat.** **Can often be separated by mechanical means.**

QUESTIONS AND PROBLEMS

1. Careful experiments show that 7 grams of iron unite with 4 grams of sulfur. How many grams of iron sulfide will be produced?

2. State the law which is applied in Problem 1.

3. What is the percentage of iron in iron sulfide? of sulfur in iron sulfide?

4. State the law illustrated in Problem 3.

5. What element have water and red oxide of mercury in common?

6. How could you prove that sugar contains the element carbon?

7. Classify the following as elements, compounds, or mixtures: bread, milk, salt, granite, lemonade, aluminum, sugar, quicksilver, brass, and sterling silver.

8. If aluminum is more abundant than iron, give some reason why iron is cheaper.

9. Why is the list of elements revised from time to time?

10. Write out a clear definition of the following terms as used in chemistry: *element*, *mixture*, *compound.*

TOPIC FOR FURTHER STUDY

Alchemy. The early chemists were called alchemists. What was their idea of an element? What was the principal aim of their experimentation? Did they succeed? (*Moore's* History of Chemistry.)

NOTE. The topics for further study will often suggest collateral reading in the history of chemistry, and the application of chemistry to industry and everyday life. A list of suggested reference books will be found in the Appendix.

CHAPTER III

OXYGEN

Importance — preparation — test — characteristics — Lavoisier's experiments on combustion — products of combustion — oxidation — speed of oxidation — spontaneous combustion — slow oxidation — kindling point — fire extinguishers — commercial uses of oxygen.

FIG. 13. JOSEPH PRIESTLEY (1733–1804).

An English clergyman who spent his last years in Pennsylvania.

17. Importance of oxygen. In our study of the elements we shall begin with oxygen. We have already met this substance as a constituent of water and of red oxide of mercury and have learned that it is the most widespread and abundant of the elements. We shall soon see that it is found in many rocks and minerals, such as sandstone and limestone, where it is combined with a great variety of other elements. Oxygen is the most active element in the atmosphere. Without it we suffocate and life is impossible. It is necessary for the production of heat since wood, coal, and gas will not burn without it; and for light wherever oil or gas is used in lamps.

18. Preparation of oxygen. In 1774 an English chemist, Joseph Priestley (Fig. 13), prepared oxygen exactly as we did in Chapter II by heating red oxide of mercury. At about the same time a Swedish apothecary, Scheele, also prepared oxygen by this method. In fact, the latter's discovery of oxygen probably antedates Priestley's, but the results were not made public until a few years later.

In the laboratory it is more convenient to heat a compound called **potassium chlorate**, which is a substance used in medicine and in making matches and fireworks. It is much cheaper than the oxide of mercury and gives, when heated, a far larger proportion of oxygen. Potassium chlorate is a white crystalline solid, a compound of the three elements potassium, chlorine, and oxygen. When it is heated to the right temperature (360° C.) * it melts, and, as the temperature rises still higher, bubbles of oxygen appear, leaving behind another compound of potassium and chlorine called potassium chloride. We can express this change in the following way:

$$\underset{\begin{bmatrix}\text{potassium}\\ \text{chlorine}\\ \text{oxygen}\end{bmatrix}}{\text{potassium chlorate}} \longrightarrow \underset{\begin{bmatrix}\text{potassium}\\ \text{chlorine}\end{bmatrix}}{\text{potassium chloride}} + \text{oxygen}$$

If we heat carefully some potassium chlorate in a test tube until it just melts and thrust a glowing spark into the test tube, we find that no oxygen is being evolved. We now drop a little black powder called **manganese dioxide** into the tube and test it again for oxygen. In spite of the fact that the tube has been slowly cooling down, oxygen is now produced. The manganese dioxide undergoes no change in this process.

A material which thus aids chemical action without being itself permanently altered is called a **catalytic agent** or a **catalyst**.

19. Some experiments with oxygen. In order to study the properties of oxygen we shall need to have it in considerable quantity.

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* The *centigrade scale* (C.) is commonly used in chemistry.

We may make it by mixing 4 parts by weight of potassium chlorate with 1 part of manganese dioxide and placing it in a thin glass flask arranged with a delivery tube (Fig. 14). The gas is collected in wide-mouthed bottles which have been previously filled with water and inverted in the pneumatic trough. When the flask is heated gently the oxygen escapes through the tube and bubbles up through the water into the bottles. The flame under the flask should be removed from time to time in order that the gas may not be too rapidly evolved and burst the flask.

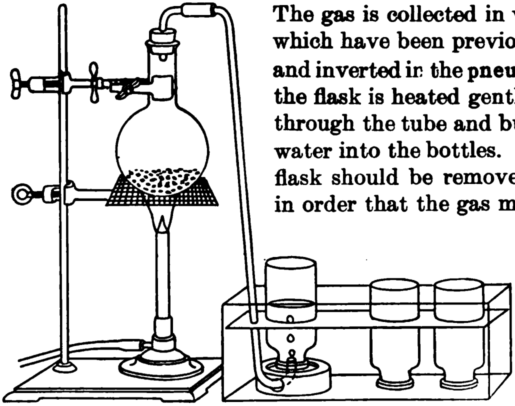

Fig. 14. Oxygen made by heating potassium chlorate and manganese dioxide.

We shall first of all convince ourselves that we have oxygen. We perform the same experiment as before (§ 9), that is, we thrust a splinter of wood with a glowing spark at one end into a bottle of the gas. The fact that the splinter bursts into flame is used as a **test** for oxygen since there is only one other gas (nitrous oxide) which behaves similarly.

We shall now study the behavior of various substances when heated in oxygen.

Charcoal: We wrap a piece of copper wire around a small bit of charcoal, heat it, and then plunge it into a bottle of oxygen; it bursts into a brilliant flame.

Sulfur: We place a bit of sulfur in an iron spoon (deflagrating spoon) and ignite it by holding it for a moment in a flame. It burns with a pale blue flame, but when put into oxygen (Fig. 15) it burns with a very brilliant light.

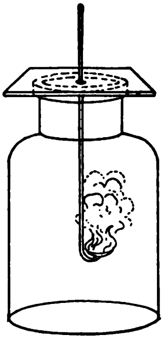

Fig. 15. Burning sulfur in oxygen.

Iron: It is possible to burn iron in oxygen if we use iron ribbon, such as a watch spring, or iron wire, such as a bunch of braided picture wire. First we coat the end with sulfur, then ignite the sulfur and suspend the wire in a bottle of oxygen. The sulfur continues to burn, producing a very intense heat which is sufficient to ignite the iron. As the iron burns it sends off a shower of brilliant sparks (Fig. 16). (It is well to cover the bottom of the bottle with a layer of sand.)

Phosphorus: This is a soft yellow substance which may take fire even at ordinary temperatures. For this reason it is always kept under water when stored. A small bit placed in a deflagrating spoon and ignited will burst into flame when placed in oxygen. The flame is so vigorous and the light so intense that one cannot look at it with comfort. The white clouds which appear are the product of the chemical reaction.

20. Characteristics of oxygen. From such experiments as these we see that the most noticeable characteristic of oxygen is that *in it substances which burn in air will burn more rapidly and with increased brilliancy.* It is a colorless gas and is so slightly soluble in water that we have no difficulty in collecting it over water. When the gas is pure it has neither smell nor taste and is slightly heavier than air.

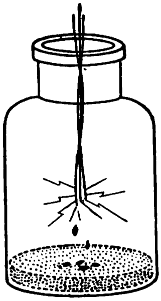

Fig. 16. Burning iron in oxygen with a shower of sparks.

Such characteristics of a substance describe its behavior and are often called the chemical properties of the substance. The mere name of a particular material tells us nothing; it is only when we know its properties that we are acquainted with it. Chemical substances are like individuals in this respect; if we know a man's name only, we know very little about him. When we have learned something about his actions and character we can tell what sort of person he is. The chemical properties of a substance describe the character of that particular kind of inanimate matter.

21. What is "burning"? We have just seen that various substances burn more rapidly in oxygen than in the atmosphere, and so we may reasonably conclude that oxygen plays an important part in the process of burning, or combustion. This is such an important chemical change that it will repay us to examine the process with considerable care and to recall in this connection some of the early experiments.

22. Lavoisier's experiment on combustion. Lavoisier (Fig. 17) was a famous French chemist who lived about 125 years ago. He is sometimes called the "father of modern chemistry" because he discovered the correct explanation of the process of burning.

FIG. 17. ANTOINE LAURENT LAVOISIER (1743–1794).

French chemist whose work laid the foundation of modern chemistry. He was a victim of the French Revolution.

He heated some mercury in a retort (Fig. 18) the neck of which extended into a jar standing in a larger dish of mercury. After heating the mercury nearly to its boiling point for several days, he discovered that *the air inclosed within the retort and jar had lost* ***one fifth*** *of its volume.* On examining the residual air he found that a lighted splint would not burn in it but was extinguished. The material in air which enables a substance to burn had evidently been removed. In the retort he found on the surface of the mercury some red powder having all the properties of the red oxide of mercury which Priestley had used for preparing oxygen.

Lavoisier now placed this in a suitable apparatus, heated it strongly, and collected the gas evolved. He obtained a gas whose volume exactly corresponded with the shrinkage undergone by the inclosed air, and in this gas substances burned with great vigor. There was now no doubt that one-fifth of the air was composed of this gas, which *Lavoisier named oxygen.* By mixing the rest of the air left in the first experiment with enough oxygen to bring it back to its original volume, Lavoisier produced a gas having all the properties of ordinary air. Thus he proved that the oxygen of the air is the only gas used up in the process of burning.

23. Products formed by burning. But if burning is a chemical reaction between oxygen and the substances burned, what about the compounds formed by the change? What has happened to them? A candle disappears almost completely when it burns. The products of the combustion in this case are gases like oxygen itself and are invisible; they can, however, be collected and weighed. When a candle burns, the compounds formed are water vapor and a gas called carbon dioxide. These so-called *products of combustion* may be absorbed by a substance known as sodium hydroxide.

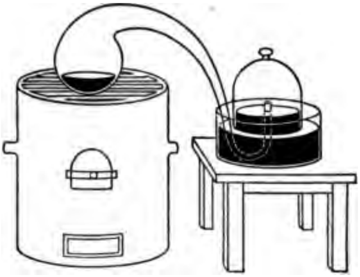

Fig. 18. Lavoisier's apparatus for studying combustion.

If we arrange a candle on a balance pan *A* and suspend above it a tube filled with sodium hydroxide, we shall be in a position to weigh both the candle and the products of combustion (Fig. 19). We carefully balance the scales by putting suitable weights on pan *B*. We then light the candle and notice that as the combustion proceeds pan *A becomes heavier* although the candle is visibly disappearing. The substances produced by the burning are *heavier* than the candle which is burned. This is because they contain the element oxygen taken from the air in addition to the elements already present in the candle.

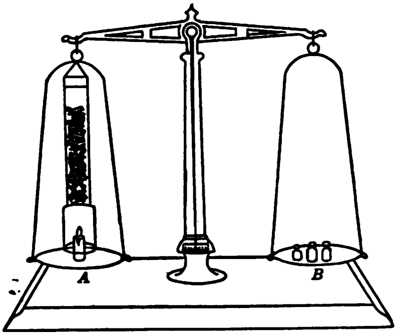

Fig. 19. The products formed by burning a candle weigh more than the candle.

This experiment shows that *if we weigh the products of combustion we always find them to be **heavier** than the substance burned.* Another experiment which illustrates the same important point is as follows:

We place some iron powder in a crucible and carefully counterpoise it on a balance with the aid of weights or small shot. We remove the crucible from the pan and heat it with a flame (Fig. 20). The mass begins to glow, showing that a chemical change is taking place. We continue the heating for about five minutes and then cool and examine the material. The crucible is found to contain a new reddish solid resembling iron rust. When the crucible is now placed on the balance pan we find that it has gained a great deal in weight. Again the increase in weight is due to the oxygen from the air which has combined with the iron to form a new compound containing the two elements iron and oxygen.

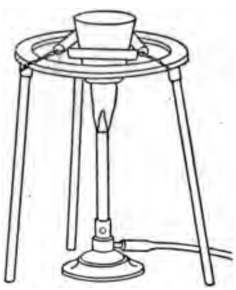

Fig. 20. Iron powder heated in a crucible gains in weight.

These experiments show that when a substance burns in air new compounds are formed by the combination of the combustible materials with the oxygen. These new compounds weigh more than the original material because they contain oxygen in addition to the combustible substances. In the case of iron the product is called iron oxide; we can represent the change as follows:

$$\text{iron} + \text{oxygen} \longrightarrow \underset{\left[\begin{smallmatrix}\text{iron}\\ \text{oxygen}\end{smallmatrix}\right]}{\text{iron oxide}}$$

An oxide is a compound of an element and oxygen. When substances burn in air or oxygen, oxides are always formed.

24. Oxidation. The reaction of a substance with oxygen is called oxidation. When this reaction proceeds so rapidly that heat and light are produced, we call the change burning, or **combustion.** Familiar examples of oxidation are the burning of coal, wood, gas, or oil, which takes place so rapidly that we have combustion. There are many cases of oxidation where the change goes on so slowly that no apparent heat or light is produced. One of the best examples of this is the rusting of iron. When iron is left in contact with the atmosphere it slowly turns into iron oxide, or, as it is commonly called, " rust." This process is hastened by the presence of water. The rusting of iron is thus exactly like the burning of wood except that in the case of iron the change takes place so slowly that no heat effect is apparent.

25. Speed of oxidation. Different substances oxidize at very different speeds. Although combustible materials combine with oxygen at all temperatures, yet in every case the speed is increased by raising the temperature. In fact, experience shows that *in every chemical change raising the temperature hastens the process.* Some substances, like phosphorus, oxidize so rapidly at temperatures only slightly higher than normal that they take fire on merely being exposed to the air. This is well illustrated by the following experiment:

Let us dissolve a little phosphorus in carbon disulfide and pour a few drops of this solution on a piece of filter paper supported on a tripod. When the solvent evaporates, the phosphorus is left widely distributed over the paper and every particle comes in contact with the air. Then the whole mass bursts into flames (Fig. 21). Under these conditions combustion starts at room temperature.

26. Spontaneous combustion. This experiment with phosphorus very well illustrates what occurs in so-called **spontaneous combustion.** Rags soaked with oils sometimes take fire when left lying about instead of being placed in a closed metal can. This is because a slow oxidation of the oil takes place on the large surface exposed to the air. The rags are poor conductors, and so the heat developed finally sets the mass on fire.

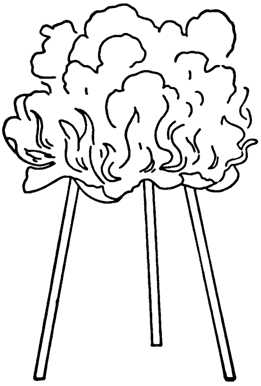

Fig. 21. Spontaneous combustion of phosphorus.

27. Kindling point. The other extreme is represented by *iron. In order to cause* this substance to burn rapidly it is necessary first to get it into a finely divided condition, then to raise it to a high temperature, and to put it into pure oxygen. We did this in a previous experiment by coating a bundle of iron wires with sulfur and bringing it to the proper temperature by the heat evolved through the rapid combustion of the sulfur in pure oxygen; under these conditions the iron itself finally caught fire and burned.

We are all familiar with the fact that coal can be made to burn only by first building a wood fire, and that the wood must in turn be ignited by paper, which again is lighted with a match. In this series the burning of each material raises the temperature of the next until it in turn finally " catches fire " and burns. The temperature at which a particular material will " catch fire " in air is sometimes called the **kindling point**. But the temperature is only *one* of the conditions which produce combustion. Finely powdered iron will start burning at a lower temperature than will an iron wire because it presents relatively more surface to the air. Besides the physical condition of the solid, the pressure of the surrounding air and the presence or absence of a catalytic agent also determine the temperature of ignition. In other words, there are several conditions which affect the kindling point.

If a mixture of oil vapor and air is raised to a certain temperature called the **flash point**, it will take fire and burn for a moment. In many states the laws require that the flash point of kerosene shall not be below 110° F. It would be dangerous to use kerosene of low flash point in lamps because its vapor mixed with air might explode.

One may burn a little gasolene in an open dish without danger; but a mixture of gasolene vapor and air may burn so quickly that it causes an explosion. Therefore *it is very important not to use such liquids as gasolene near an open flame* since they evaporate rapidly and the vapor with air forms an explosive mixture.

28. Extinguishing fire. When we wish to put out a fire we try to cool the burning material below its kindling point by pouring water on it. This usually succeeds if we have sufficient water at hand. All methods of extinguishing fire depend either upon cooling the combustible material or upon excluding the air so that oxygen is no longer available for the oxidation. If we use water we combine the two advantages, although water acts chiefly by cooling the burning material. Sand and gravel, which are used to extinguish certain kinds of fires, such as burning gasolene, simply smother the fire by excluding the air. So-called chemical fire extinguishers, as we shall see in Chapter VII, combine the cooling effect of a liquid with the smothering effect of a heavy non-combustible gas which hangs like a cloud over the burning material and excludes the air.

29. Commercial uses of oxygen. The oxygen of commerce is now usually made from **liquid air**, which will be described in section 78. The liquid oxygen boils at −182.4° C., but the nitrogen boils even at a lower temperature (−194° C.). Therefore the latter evaporates more freely than does the oxygen. When the liquid is almost pure oxygen (about 96 per cent), the gas is pumped into steel cylinders (Fig. 22). Physicians sometimes use oxygen for patients who are suffering from pneumonia or suffocation. It is also used instead of air when intense heat is required, as in the acetylene torch and calcium light. Oxygen in tanks is used to restore the supply in the atmosphere of submarine boats. It has recently been found that the aviators who ascended to high altitudes, such as 19,000 feet, where the air is rarefied, get only half the usual amount of oxygen and so become "dopey." An equipment has therefore been designed to supply the needed oxygen from a tank through a connecting tube to a face mask covering the mouth and nose. All military airplanes flying over an altitude of 10,000 feet are now equipped *for the use of artificial oxygen.*

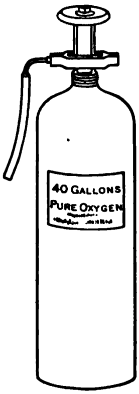

Fig. 22. Steel cylinder of oxygen under pressure.

SUMMARY OF CHAPTER III

OXYGEN CAN BE PREPARED BY:

(*a*) heating red oxide of mercury (historic);
(*b*) heating potassium chlorate (laboratory);
(*c*) evaporating liquid air (commercial).

A CATALYST is a substance which is not itself altered but which causes a chemical change to take place more easily. The addition of manganese dioxide to potassium chlorate makes the oxygen come off at a lower temperature.

OXYGEN is a colorless odorless gas somewhat heavier than air. It combines with nearly all other elements.

OXIDATION is the process of combining a substance with oxygen.

AN OXIDE is a compound of oxygen and another element. Oxides are formed when an element burns in oxygen or air.

COMBUSTION is a chemical action in which heat and light are produced.

ORDINARY BURNING is a rapid oxidation which is accompanied by heat and light.

THE KINDLING POINT of a material is the lowest temperature at which it takes fire and burns.

SPONTANEOUS COMBUSTION occurs when material is raised to its kindling point by the heat produced through a slow oxidation which starts at ordinary temperatures.

THE SPEED of all chemical changes is increased by raising the temperature.

QUESTIONS

1. Name three metals which do not oxidize.

2. How could you prove experimentally that part of the air disappears in the rusting of iron?

3. Assume that potassium chlorate is 39% oxygen. If 12 grams of potassium chlorate and 3 grams of manganese dioxide are used to produce oxygen, how much of each product is left in the flask?

4. Explain why wood in the form of shavings burns more rapidly than the same wood in the form of a log.

5. Would oxygen burn in an atmosphere of illuminating gas?

6. Why does coal packed closely in poorly ventilated bunkers often take fire?

7. Why is oxygen sometimes called a *supporter* of combustion?

8. When metals tarnish or rust, do they change in weight?

9. Why does a good draft make a fire burn more rapidly?

10. Why does blowing extinguish a candle?

11. What is the danger in letting the wind blow out a gas flame?

12. Why do we not fill balloons with oxygen?

13. How would you distinguish a bottle of oxygen from a bottle of air?

14. How would you prove that ordinary tap water contains dissolved oxygen?

15. What is the safe way to dispose of greasy cloths?

16. If your clothing caught on fire how would you put it out?

17. Why do firemen and miners use oxygen helmets?

18. Why are buildings sometimes dynamited to stop a conflagration?

19. Name three cases of practically instantaneous combustion.

TOPICS FOR FURTHER STUDY

Fire prevention. The loss of life and property by fire is a very serious matter in the modern world. State and municipal governments have passed laws tending to prevent the outbreak of fire. What are the " fire laws " in your community? What means are provided for extinguishing fires? What are the relative advantages of different kinds of fire-fighting apparatus, such as the " hand engine," the " steamer," the " chemical engine," and a high-pressure system? What are the modern methods of fireproof construction? What are automatic extinguishers?

Early American chemists. Why is the life of Priestley of especial interest to Americans? Who were some of the early American chemists, and what did they accomplish? (*Moore's* History of Chemistry and *Smith's* Chemistry in America.)

CHAPTER IV

HYDROGEN

Occurrence — preparation from water and acids — displacement — purification — experiments to illustrate its properties — chemical behavior — reducing agent — uses.

30. Where hydrogen is found. We have just studied one of the elements in water — oxygen; in this chapter we shall deal with the other element — hydrogen. This element is also a gas, but unlike oxygen it does not occur to any extent in a free state in nature. It is found in small amounts as one of the constituents of natural gas, an inflammable mixture of gases which issues from the ground in certain parts of the world. Nearly three-fourths of the illuminating gas used in this country is water gas, which is about 38 per cent hydrogen. It is also present in combination with other elements in plants, animals, and in the human body.

31. Preparation from water. We have already (§ 19) seen that iron, when heated to a moderately high temperature, combines with oxygen. If we heat iron wire red-hot in a porcelain or iron tube and then pass steam through the tube, the hot iron combines with the oxygen in the steam, setting free the hydrogen, which may be collected. The chemical change involved in this experiment may be represented as follows:

$$\text{iron} + \underset{\left[\begin{smallmatrix}\text{hydrogen}\\ \text{oxygen}\end{smallmatrix}\right]}{\text{water}} \longrightarrow \text{hydrogen} + \underset{\left[\begin{smallmatrix}\text{iron}\\ \text{oxygen}\end{smallmatrix}\right]}{\text{iron oxide}}$$

Hydrogen can be obtained from water even at ordinary temperatures by means of certain metals. Thus, if a small bit of metallic sodium is dropped on water, action begins at once.

The metal is very light and runs hissing about on the surface of the water. As the action often ends with a slight explosion a glass plate should be held up to protect the eyes. We may collect the hydrogen which is evolved by the action of sodium on water as follows:

Let us take a short piece of small lead pipe (about 1 inch long and ¼ inch bore) with one end hammered together, and fill it with freshly cut sodium. If we drop this tube with its charge of sodium into a dish of water, bubbles rise and may be collected in an inverted cylinder filled with water (Fig. 23).

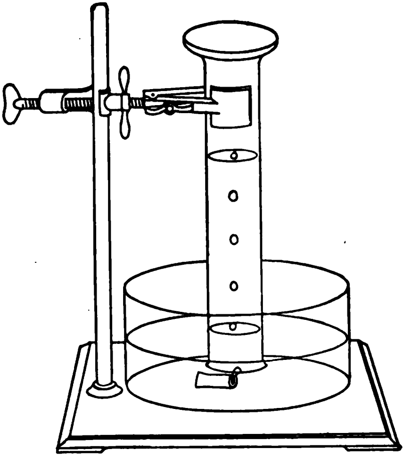

Fig. 23. **Metallic sodium in water generates hydrogen.**

If potassium is used the action is more violent and so much heat is generated that the hydrogen is set on fire. When calcium is used the metal sinks to the bottom of the vessel, so that a bottle filled with water can easily be inverted over the metal to collect the gas as it is formed. In each of these cases *the metal displaces only one-half of the hydrogen in the water;* it combines with the remaining half and with all of the oxygen to form the compound known as the **hydroxide** of the given metal. The chemical reaction of sodium and water may be expressed thus:

$$\text{sodium} + \underset{\begin{bmatrix}\text{hydrogen}\\ \text{oxygen}\end{bmatrix}}{\text{water}} \longrightarrow \text{hydrogen} + \underset{\begin{bmatrix}\text{sodium}\\ \text{hydrogen}\\ \text{oxygen}\end{bmatrix}}{\text{sodium hydroxide}}$$

The sodium hydroxide and potassium hydroxide are very soluble in water, but most of the calcium hydroxide is not dissolved and may be seen suspended in the water.

32. Action of metals on acids. The most convenient way of preparing hydrogen in the laboratory is by the action of certain metals on acids. Acids are compounds which contain hydrogen and which have certain peculiar properties which we shall consider in another chapter. The commonest acid is **sulfuric**, often called "oil of vitriol." It is a heavy liquid which mixes with water in all proportions. The pure liquid is known as **concentrated** sulfuric acid; when it is mixed with four or five times its volume of water, it is known as **dilute** sulfuric acid. Dilute sulfuric acid reacts vigorously with commercial granulated zinc, producing hydrogen. If the zinc and the acid are pure the action is very slow and must be catalyzed by adding a little copper sulfate solution to the acid.

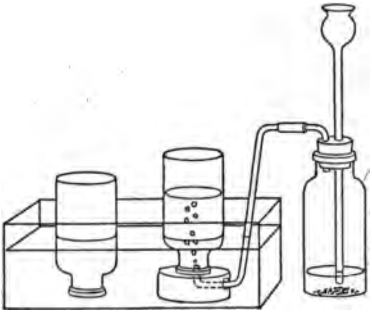

Fig. 24. Apparatus for generating hydrogen by the action of an acid on zinc.

The zinc is placed in a bottle fitted with a two-hole stopper (Fig. 24). A long thistle tube reaches to the bottom of the bottle and is used to introduce the acid and also as a safety tube. The other tube serves to conduct the hydrogen through the tube into the pneumatic trough. After the apparatus is assembled the acid is poured through the thistle tube and the action starts at once; a copious stream of gas bubbles through the pneumatic trough and may be collected in bottles.

The reaction which takes place in this case may be represented as follows:

$$\text{zinc} + \underset{\begin{bmatrix}\text{hydrogen}\\ \text{sulfur}\\ \text{oxygen}\end{bmatrix}}{\text{sulfuric acid}} \longrightarrow \text{hydrogen} + \underset{\begin{bmatrix}\text{zinc}\\ \text{sulfur}\\ \text{oxygen}\end{bmatrix}}{\text{zinc sulfate}}$$

The other product of the reaction, zinc sulfate, is a white solid which is soluble in water and can be obtained if the liquid left in the bottle is evaporated. It will be noticed that the element zinc has taken the place of the hydrogen in the sulfuric acid, liberating the hydrogen as the free element. This is a new kind of chemical change; it is known as **displacement.** Here *an element displaces one of the elements from a compound, setting it free, and unites with the rest of the constituents of the compound.*

Other metals besides zinc, such as magnesium, aluminum, and iron, may be used to displace the hydrogen of dilute sulfuric acid. Other acids, such as dilute hydrochloric acid, may be used instead of sulfuric.

33. Purification of hydrogen. When iron is used to prepare hydrogen, the gas has a distinct odor, due to the impurities usually present in iron wire or filings. Even when commercial zinc and acid are used, the impurities carried along give it a disagreeable odor. We may remove most of the impurities by passing the gas through a suitable solution containing sodium hydroxide and potassium permanganate, and then we may absorb the water vapor by the use of a drying agent, such as granular calcium chloride. Hydrogen when pure is a gas without color, taste, or odor.

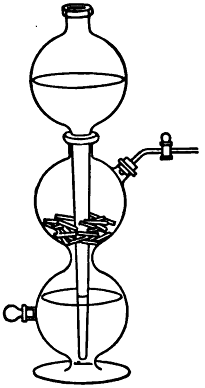

Fig. 25. Kipp generator.

34. Experiments with hydrogen. A steady stream of hydrogen can be conveniently produced by a Kipp generator. This apparatus (Fig. 25) is so arranged that it contains a small reserve of hydrogen in the middle bulb. When this reserve is drawn on by opening the stopcock, fresh acid automatically rises and acts on the zinc which is also in the middle bulb; this action replenishes the supply of gas. If too much gas is generated the acid is forced away from the zinc and the action stops. In this way a steady stream of gas is delivered.

First we shall take a wide-mouthed bottle filled with hydrogen and apply a flame to its mouth; if the hydrogen is mixed with air, a slight pop results, but if free from air it burns quietly.

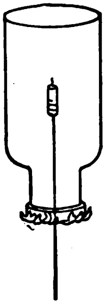

Fig. 26. Hydrogen burns but the taper does not burn in it.

If we lift up another bottle of hydrogen and hold it mouth down while we insert a lighted taper (Fig. 26), we find that the hydrogen burns around the mouth of the bottle and the taper is extinguished. On being withdrawn the taper is again lighted in passing through the burning hydrogen. The operation may be repeated several times until the hydrogen is burned up. This striking experiment shows *that hydrogen does not " support combustion."*

To show how very light hydrogen is we may attach a common clay pipe to a hydrogen generator and dip the bowl in a soap solution. We may thus fill soap bubbles with the gas (Fig. 27). When disengaged from the pipe each bubble rises rapidly in the air. The gas is so light that a soap bubble filled with it can lift another containing air (Fig. 28).

Another striking experiment which illustrates this same point is as follows: suspend an inverted beaker from one arm of a balance and then *pour hydrogen up into it* (Fig. 29). The beaker rises.

We shall next mix equal volumes of air and hydrogen by bringing a bottle when only half full of hydrogen up out of the pneumatic trough so that air takes the place of the water. When a flame is brought near such a mixture of gases there is a loud explosion.

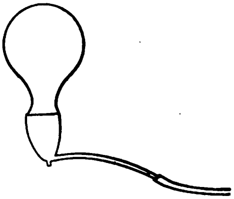

Fig. 27. Soap bubbles filled with hydrogen.

When we have hydrogen unmixed with air we may attach to the generator a clay-pipe stem to serve as a jet and may light the hydrogen. The flame is very hot but gives no light; it is almost without color, being only slightly bluish.

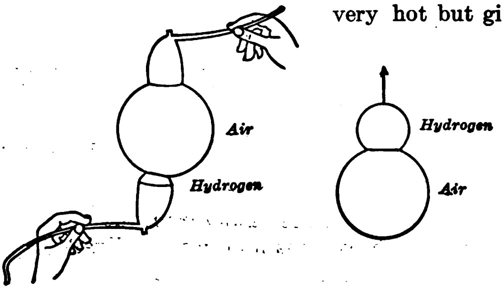

Fig. 28. Hydrogen bubble lifting another bubble filled with air.

In order to study the product of burning hydrogen in air we attach a drying tube filled with calcium chloride between the jet and the generator. When all the air has been expelled from the apparatus, the hydrogen burns with a small flame. If we hold a cold, dry bell jar over the flame, as shown in figure 30, water vapor is soon seen condensing on the jar, and after a short time drops of water run down the sides.

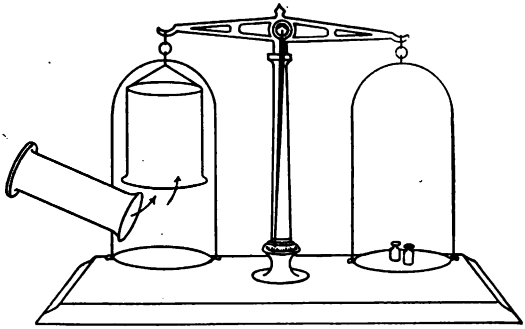

Fig. 29. Pouring hydrogen up into an inverted beaker.

35. Properties of hydrogen. In such experiments we have observed some of the characteristics of hydrogen. Like oxygen, when pure it is a colorless, odorless gas. It is sixteen times lighter than oxygen, being in fact the lightest of all known substances. Since hydrogen is so light a gas it escapes through small apertures most rapidly. This is the reason why a small rubber balloon filled with hydrogen collapses more rapidly than a similar balloon filled with illuminating gas. The solubility of hydrogen in water is very slight, being even less than that of oxygen.

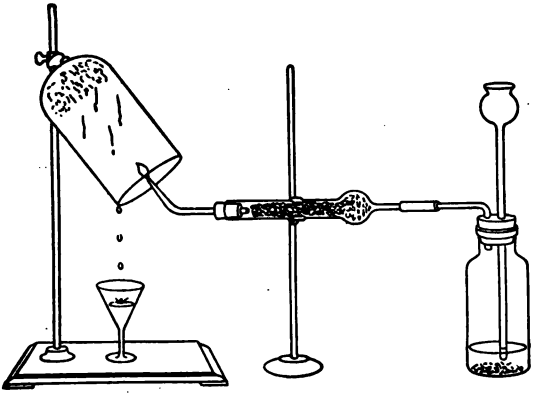

Fig. 30. Water is formed by burning hydrogen.

Hydrogen can be liquefied by compression provided it is first cooled below its critical temperature* (−234° C.). Liquid hydrogen is also colorless and when allowed to evaporate rapidly it freezes to a colorless solid.

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* The critical temperature of a gas is the temperature below which it must be cooled *before it can be liquefied* by any pressure however great.

36. Chemical behavior of hydrogen. We have seen that hydrogen burns in the air, and we have already learned that the process of burning is the rapid union of a substance with the oxygen of the air; we have also learned that when elements burn oxides are formed. So in the case of burning hydrogen the product is the familiar compound of hydrogen and oxygen — water:

$$\text{hydrogen} + \text{oxygen} \longrightarrow \text{water}$$

Although hydrogen is itself readily combustible yet *it is not a supporter of combustion;* that is, substances will not burn in it. At ordinary temperatures hydrogen is not an active element. But under certain conditions it does combine with many of the elements. For example, if a mixture of hydrogen and chlorine is exposed to the sunlight the two gases will combine with explosive violence to form *hydrogen chloride.* Under the right conditions hydrogen combines with nitrogen to form *ammonia* and with sulfur to form *hydrogen sulfide,* which is the gas that is characteristic of rotten eggs. If a mixture of hydrogen and oxygen is heated to about 800° C. a violent explosion occurs and water is formed.

We may prepare a mixture consisting of two volumes of hydrogen and one volume of oxygen (§ 57) and pass it into soapy water so that a froth of bubbles filled with the mixture is formed. We first *remove the generator* and then set the froth on fire with a long gas-lighting taper. The mixture burns with a report like the shot of a gun.

Although at a comparatively high temperature the combination of hydrogen and oxygen takes place with great violence, yet these two gases can be left together at room temperature for a very long time without chemical action. If, however, we introduce certain metals, such as finely divided platinum, chemical reaction sets in, and sometimes the platinum becomes so warm that it glows from the heat produced by the combination. The platinum undergoes no change, it merely acts as a **catalyst**. We may think of the catalyst as acting like oil which is applied to a machine as a lubricant. We grease the bearings to make the wheels go around more easily; we add a catalyst to make a chemical change take place at a lower temperature.

37. Reducing action. Hydrogen will not only combine with gaseous oxygen when heated, but will remove oxygen from many compounds.

Copper oxide is a black solid consisting of the two elements copper and oxygen. It may be formed by heating metallic copper in the air. This oxidation proceeds slowly and gradually converts all the elementary copper into the oxide.

The apparatus shown in figure 31 is so arranged that dry hydrogen may be passed over hot copper oxide. The oxide is placed in the glass tube and heated with a burner until it is almost red-hot. Hydrogen is then passed over it. Water is formed and condenses in the tube. Metallic copper is left in the tube and can be recognized by its reddish color and metallic luster.

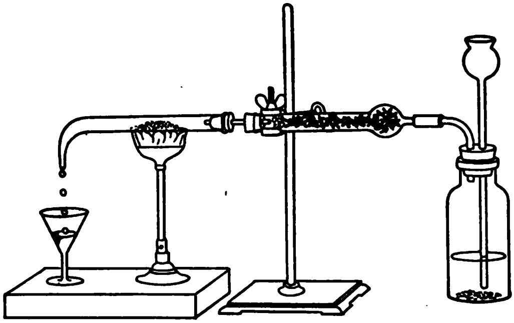


Fig. 31. Dry hydrogen is passed over hot copper oxide.

When hydrogen combines with the oxygen of a compound and thus removes it, we say the substance has been **reduced**. *Reduction is therefore essentially the removal of oxygen.* During this process the hydrogen has combined with the oxygen, forming water. This change can be expressed thus:

$$\underset{\left[\begin{smallmatrix}\text{copper}\\ \text{oxygen}\end{smallmatrix}\right]}{\text{copper oxide}} + \text{hydrogen} \longrightarrow \underset{\left[\begin{smallmatrix}\text{hydrogen}\\ \text{oxygen}\end{smallmatrix}\right]}{\text{water}} + \text{copper}$$

The combining of a substance with oxygen we have previously defined as **oxidation**. Therefore the hydrogen has been oxidized, the copper oxide has been reduced. ***Reduction is always accompanied by oxidation.*** If one substance is reduced, some other substance must be oxidized. Besides hydrogen there are other substances, such as carbon, which act as reducing agents, and we shall later see that the terms "oxidation" and "reduction" are often given a somewhat wider meaning.

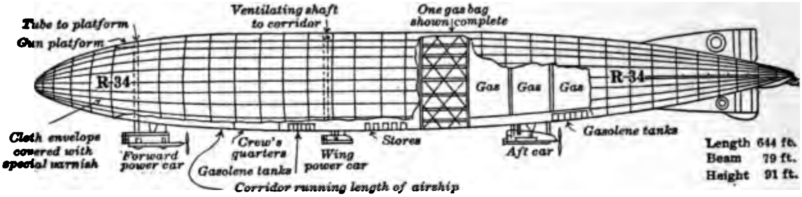


Fig. 32. Dirigible airship R-34 which crossed the Atlantic.

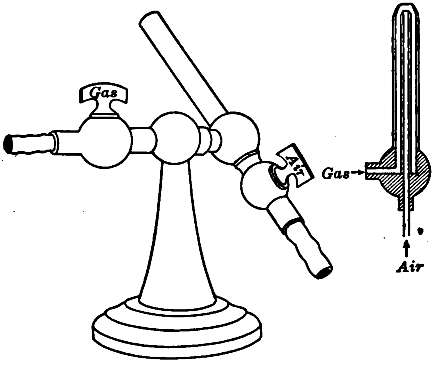


Fig. 33. Blast lamp.

38. Uses of hydrogen. Hydrogen gas has a few practical applications. Because it is the lightest known gas it is used to fill balloons and dirigible airships (Fig. 32). It also enters into the process by which certain vegetable and animal oils are changed into hard fats. This process is called *hydrogenation* and will be described in Chapter XXIV. Hydrogen for commercial purposes is usually prepared by the electrolysis of water. This process was explained in Chapter II.

The flame of burning hydrogen is very hot and is particularly so if oxygen is forced into it in a suitable burner. This burner is very similar to that shown in figure 33, which is an ordinary **blast lamp** using illuminating gas and air instead of hydrogen and oxygen. The oxyhydrogen flame was formerly much used when a very intense heat was desired. It has largely been supplanted by the oxyacetylene flame and the electric arc.

SUMMARY OF CHAPTER IV

HYDROGEN MAY BE PREPARED by:

(*a*) reaction between water and a metal;
(*b*) displacement in an acid by a metal
(usual laboratory method);
(c) electrolysis of water (commercial method).

HYDROGEN IS a *colorless, odorless* gas. It is the *lightest* known gas.

HYDROGEN BURNS in oxygen or air, forming water. It is a powerful *reducing* agent. When a substance is reduced by hydrogen, the hydrogen in turn is *oxidized*. Reduction is always accompanied by oxidation.

THE CHIEF USE of hydrogen is to fill balloons and dirigibles. It is also used for the hydrogenation of oils. The oxyhydrogen flame was formerly used to produce intense heat.

QUESTIONS

1. In what properties are hydrogen and oxygen alike? In what are they unlike?

2. What property has hydrogen which makes it a dangerous substance with which to inflate balloons?

3. How would you test hydrogen to see if it were contaminated with air?

4. How would you keep a bottle of hydrogen overnight?

5. Could pure hydrogen be used in a Bunsen burner instead of illuminating gas?

6. What is the essential difference between oxides and hydroxides?

7. In the experiment of burning hydrogen to form water, why *is it necessary to dry the hydrogen?*

8. Why is oxygen passed through the inner tube of the oxyhydrogen blowpipe rather than the outer?

9. Do we ever have oxidation without reduction?

10. Name the three types of chemical reactions which have been studied thus far and describe briefly an example of each.

11. Is it necessary to use a pneumatic trough in collecting hydrogen?

12. Explain how the thistle tube in the hydrogen generator acts as a safety tube.

13. Hydrogen can be ignited by holding finely divided platinum in a jet of the gas. Explain.

TOPIC FOR FURTHER STUDY

Dirigible airships and balloons. What are the relative merits of dirigibles and airplanes? What were balloons used for in the World War? What properties of hydrogen make it valuable for balloons? What properties make it undesirable? Have any other gases been used to fill balloons? (*Cressy's* Discoveries and Inventions, and *Tilden's* Chemical Discovery and Invention.)

CHAPTER V

GASES AND THEIR MEASUREMENT

What is the density of a gas — standard conditions — atmospheric pressure — effect of pressure on volume, Boyle's Law — effect of temperature on volume, Law of Charles — absolute temperature scale — gas equation — correction of pressure for water vapor — kinetic molecular theory.

39. How to get the density of a gas. One of the important properties of any substance is its **density.** In the case of a solid or liquid we have only to weigh a definite volume and then compute the *weight of a unit volume*, that is, the number of grams per cubic centimeter. But in determining the density of a gas, such as air, oxygen, or hydrogen, we have a much more difficult problem. This is because gases are all very light and therefore hard to weigh, and also because a gas has no definite volume since it always fills the containing vessel. Then, too, the volume of gases is very much influenced by the temperature and pressure to which they are subjected. The principle, however, is just the same as with solids and liquids: we weigh a given volume of a gas under known conditions of temperature and pressure, then compute what the volume would be under standard conditions, and finally calculate the weight per unit volume, usually the number of grams per liter.

40. Standard conditions. The relative densities of various gases are especially important to the chemist both theoretically and practically. It is necessary first, however, to fix on certain standard or normal conditions of temperature and pressure. Chemists have generally agreed that *zero degrees centigrade (0° C.) and 760 millimeters (mm.) pressure* shall be considered

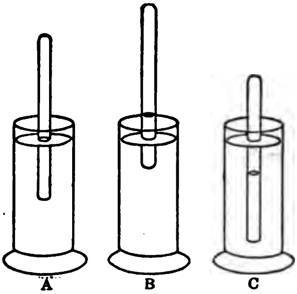


Fig. 34. Differences of level affect volume of gas.

the standard temperature and pressure for gases. Not that we shall always endeavor to measure gases at 0° C. (the temperature of melting ice) and 760 mm. (the average pressure of the atmosphere at sea level); but simply that, knowing the actual temperature and pressure, we shall calculate what the volume of the gas would be under these standard conditions.

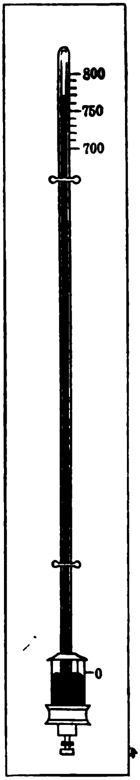


Fig. 35. Mercurial barometer for measuring atmospheric pressure.

41. Measurement of atmospheric pressure. Since we usually collect gases over water in a pneumatic trough and make the level of the water inside the measuring jar or bottle the same as that of the water outside (Fig. 34 *A*), we are subjecting the gas to atmospheric pressure. To measure the pressure of the atmosphere we have simply to read the barometer. The mercurial barometer (Fig. 35) consists of a column of mercury which just balances the pressure of the atmosphere. Usually the instrument consists of a stout glass tube about a meter long, closed at one end. This has been completely filled with mercury and then inverted so that the open end projects into a cup or reservoir of mercury. The mercury in the tube sinks to a level about 760 millimeters above the mercury surface in the cup. The space above the mercury in the tube is empty except for a minute quantity of mercury vapor; in fact, it is the most perfect vacuum that we know how to make. To "read the barometer" means simply to measure accurately the height of the mercury column above *the surface of the liquid* in the reservoir. Such a barometer indicates the variations in atmospheric pressure from day to day due to fluctuations in the atmosphere itself; it also indicates changes of pressure due to changes in the elevation of the observer.

42. How the volume of a gas changes with pressure. In order to compute what the volume of a given weight of gas would be under standard conditions, we must first find out how much the volume of a gas varies as the pressure changes. This was first investigated for the case of air by an Irishman, Boyle (Fig. 36), and a few years later by a Frenchman, Mariotte. The results of their experiments showed that if we start with a given volume of air subjected to a certain pressure and then double the pressure, the volume of air will be reduced to one-half. If the pressure is made three times as great, the volume of the air will be reduced to one-third, provided the temperature of the air is kept constant. This was found to be a general principle which applies to all gases. It is known as BOYLE'S LAW and may be stated as follows: *The volume of a gas at constant temperature varies inversely as the pressure.*

FIG. 36. ROBERT BOYLE (1626–1691).

Pioneer investigator in physics and chemistry; studied effect of pressure on volumes of gases; first to realize the difference between elements and compounds.

This may also be expressed in symbols, thus:

$$V : V' :: P' : P$$

(note the inverse proportion)

or

$$PV=P'V' \tag{I}$$

where V and V' denote volumes of a given quantity of gas kept at some fixed temperature, and P and P' denote the corresponding pressures.

It is easy to illustrate this law by an experiment. Suppose we arrange a graduated glass tube T as shown in figure 37. This is connected by a rubber tube to a small reservoir of mercury which may be raised and lowered. First we place the reservoir in such a position that the mercury in it is exactly level with that in the tube. In this position the air in the tube is under atmospheric pressure. We note the volume of air. Next we raise the mercury reservoir and compress the air until its volume is reduced to one-half. When it reaches this point we find by measurement that the height of the mercury in the reservoir above that in the tube is about 760 mm. (or whatever the barometer reads). Hence, we have subjected the gas within the tube to the pressure of an additional atmosphere; in other words, there is now *twice* the pressure upon it that there was at first, and its volume is reduced to *one-half*.

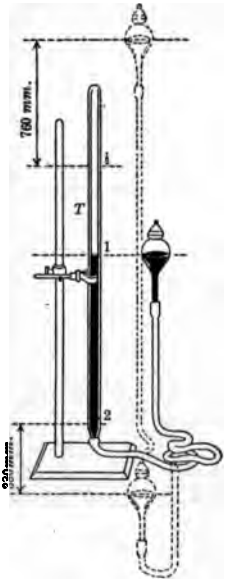


Fig. 37. Apparatus for illustrating Boyle's Law. Pressure is varied by raising and lowering mercury reservoir.

In the same way, if the reservoir be lowered until the gas in the tube has expanded to twice its original volume, we shall find on measuring that the mercury in the reservoir stands 380 mm. below that in the tube. Instead of being under ordinary atmospheric pressure, the gas is now under *reduced* pressure. It is subjected to a pressure of 760 mm. – 380 mm. or 380 mm. In other words, the pressure is only *half* the ordinary atmospheric pressure, and the volume of the gas is *doubled*.

43. Use of Boyle's Law in the correction of gas volumes. Suppose a quantity of oxygen has a volume of 1200 cc. and the barometer stands at 740 mm. What will be the volume under *standard pressure (760 mm.)?*

According to Boyle's Law

$$PV = P'V'$$

Substituting the values given in the problem, we have

$$760\ V = 740 \times 1200$$

or $$V = 1169 \text{ cc.}$$

It will serve as a useful check on this result to note that the gas under standard pressure will be subjected to a greater pressure than before, and accordingly its volume will be less.

NOTE. In solving such problems in chemistry it will save much time to use a four-place logarithmic table or, better still, a slide rule. Generally it is sufficiently accurate to get three significant figures (§ 115) in the answer.

PROBLEMS

1. What volume will 45 cc. of hydrogen occupy when its pressure changes from 770 mm. to 750 mm.?

2. If 380 cc. of oxygen were measured at 745 mm. pressure, what would be the volume at 760 mm.?

3. A gas under a pressure of 60 cm. has a volume of 645 cc. What will be its volume under a pressure of 80 cm.?

4. If a certain quantity of gas under standard pressure (760 mm.) occupies 950 cc., find what volume it would occupy when subjected to a pressure of 77 cm.

5. Oxygen is sold in steel cylinders under a pressure of 150 pounds per square inch. As the gas is used the pressure drops. When it has dropped to 30 pounds, what fractional part of the original gas remains?

44. How the volume of a gas changes with the temperature. We all know that nearly everything expands when heated. For example, the mercury or alcohol in a thermometer expands and so rises in the stem when warmed. But perhaps we are not familiar with the fact that gases when warmed expand *much more than liquids;* thus, air expands about nine times as much as water. Even more remarkable, however, is the fact that all gases expand at nearly the same rate.

By the following experiment it is easy to measure in a rough way the amount which gases expand. Suppose we take a glass tube of uniform bore (about 1 or 2 mm. in diameter) which has been closed at one end and which contains a little pellet of mercury to separate the inclosed gas *AB* (Fig. 38) from the atmosphere. (Dry air is a good gas with which to experiment.) If we put the tube down into a pail of cracked ice (a freezing mixture at 0° C.), the gas in the tube will contract and we can measure this length *AB* of the column of gas, which we shall assume to be 273 mm. If we put the tube into steam at 100° C., the gas will expand and we can measure its length again. This length *AB′* we shall find to be about 373 mm. From this experiment we see that the air expanded 1 mm. for each degree rise in temperature (the expansion of the glass can be neglected). That is, *the gas has expanded* $\frac{1}{273}$ *or 0.00366 of its volume at 0° C. for each degree rise in temperature.*

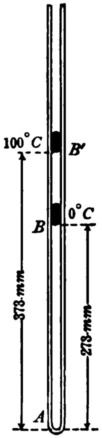


Fig. 38. Tube containing dry air and a pellet of mercury.

45. Absolute temperature scale. In the experiment just described we started with an air column 273 mm. in length at 0° C.; if we had cooled the gas from 0° C. to −1° C., the length would have been shortened a millimeter; and if we had cooled it to −10° C., the length of the air column would have become 263 millimeters. If, then, the air column continued to contract at the same rate when cooled indefinitely, the volume of the air at −273° C. would become zero. As a matter of fact, we can never get a gas to so low a temperature as −273° C., because every known gas turns into a liquid before that temperature is reached. This temperature −273° C. is, however, one of unusual interest in the study of gases. It is called the **absolute zero**, and temperatures measured from this point as zero are called **absolute temperatures**. Absolute temperatures may be designated by the letter A. Thus, 0° C. is 273° A., *50° C. is 323° A., and 100°* C. is 373° A. To change any temperature from the centigrade to the absolute scale, we have merely to add 273 degrees (Fig. 39).

The peculiar interest which this new thermometer scale has for the chemist lies in the fact that the volumes which a given weight of gas occupies at two different temperatures are directly proportional to the absolute temperatures. From this discussion of absolute temperatures it will be seen that the volume of any gas is doubled when its temperature is raised from 273° A. (0° C.) to 2 × 273° or 546° A. (273° C.).

46. The Law of Charles. A little more than a century ago a Frenchman, Charles, studied the expansion of gases under constant pressure and discovered that all gases expand and contract to the same extent under the same changes of temperature, provided there is no change in pressure.

In general, the volume of a gas is very nearly proportional to its absolute temperature when the pressure is kept constant. This is known as the LAW OF CHARLES.

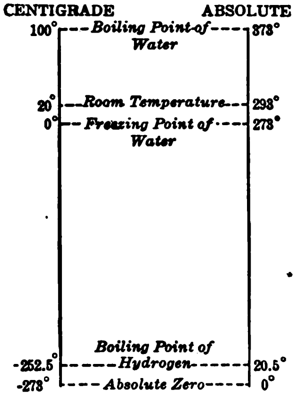


Fig. 39. Centigrade and absolute temperature scales.

This relation between the volume and temperature of a gas can be very concisely expressed algebraically:

$$\frac{V}{V'}=\frac{T}{T'} \qquad \text{II}$$

where V and V' represent the volumes of a certain quantity of gas at the same pressure but at different absolute temperatures, T and T'. If t is the temperature on the centigrade scale when the volume is V, then $T=273+t$; similarly, $T'=273+t'$.

FOR EXAMPLE, suppose we have a quantity of gas which measures 320 cc. when the temperature is 15° C. What volume will this occupy *at 0° C.?*

First change the centigrade temperatures given in the problem to absolute temperatures by adding 273 and then substitute in the equation for the Law of Charles:

$$\frac{V}{320} = \frac{273}{273 + 15}$$

or

$$V = \frac{320 \times 273}{288} = 303 \text{ cc.}$$

In solving such problems the student would do well to compare his result with the original volume to see whether it is reasonable. If the temperature of a gas measured in the laboratory is 20° C., then the gas under standard conditions would contract about 7 per cent.

Problems

1. What volume would 160 cc. of oxygen, measured at 17° C., occupy at 0° C.?

2. If 250 cc. of gas were measured at –10° C., what will be the volume at standard temperature?

3. A quantity of gas occupies 100 cc. when measured at 0° C. What will it measure when heated to 30° C.?

4. Given 560 cc. of hydrogen measured at 10° C. If the gas is heated to 20° C., how many cubic centimeters will it then occupy?

5. What change in volume would occur if 2 liters of gas at 200° C. were cooled to 0° C.?

47. The gas equation. In practice the chemist usually has to make corrections for *both* the pressure and the temperature in reducing his volume of gas to standard conditions. It will therefore be helpful to combine the Laws of Boyle and Charles into one equation:

$$\frac{PV}{T} = \frac{P'V'}{T'} \qquad \text{III}$$

It will readily be seen that this equation reduces to equation I (Boyle's Law) when $T = T'$, and that if $P = P'$ the equation becomes $V/T = V'/T'$, which is another form of equation II (Charles' Law). Equation III is called the **gas equation.**

For example, suppose we wish to find the volume of a certain quantity of gas under standard conditions, that is, at 0° C. and 760 mm. pressure, when it is known to occupy 1200 cc. at 15° C. and under a pressure of 740 mm.

Substituting in equation III we have

$$\frac{1200 \times 740}{273 + 15} = \frac{V' \times 760}{273 + 0}$$

whence

$$V' = \frac{1200 \times 740 \times 273}{760 \times 288} = 1110 \text{ cc.}$$

48. Correction for water vapor. As we have said, the chemist in the laboratory usually collects gases over water, and in this case there is one more correction to be applied. When a gas is collected over water and the level of the water is the same within and without the measuring vessel, the inclosed gas is under atmospheric pressure. But to some extent water has evaporated into the vessel, and a part of the volume inclosed is due to the water vapor and not to the gas. This water vapor exerts a certain pressure, depending on the temperature.

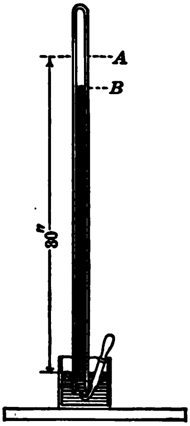


Fig. 40. Mercury column with drop of water on top.

We may demonstrate this pressure of water vapor by the following experiment: We take a strong glass tube (about 90 cm. long) closed at one end and fill it completely with clean mercury. If we close the opening with the finger, we may invert it in a small dish of mercury. Then we introduce into the vacuum above the column of mercury a drop of water with a medicine dropper, as shown in figure 40. The drop *AB* in the mercury column is equal to the pressure of the water vapor and increases as the temperature rises.

Therefore the pressure inside a bottle of gas collected over water is the pressure of the gas *plus* the water-vapor pressure, while outside it is simply atmospheric pressure. What we want, however, is simply the pressure exerted by the gas collected. Since we cannot easily remove the water vapor, we can do what amounts to the same thing. *We subtract the pressure of the water vapor* (aqueous tension), *expressed in millimeters of mercury, from the barometric pressure,* and the result is the ***corrected pressure.*** This we use in our calculation.

NOTE. — A table in the Appendix gives the pressures due to water vapor at various temperatures.

FOR EXAMPLE, suppose a gas measured 300 cc. over water when the barometer read 740 mm. and the temperature was 25° C. What would be its volume under standard conditions?

From the table for aqueous tension we see that the pressure of water vapor at 25° C. is 24 mm.; therefore the corrected pressure is 740 − 24, or 716 mm.

Substituting in the gas equation, we have

$$\frac{300 \times 716}{298} = \frac{V' \times 760}{273}$$

whence $$V' = 259 \text{ cc.}$$

PROBLEMS

1. A gas measured 1050 cc. at 740 mm. and 22° C. What would be its volume under standard conditions?

2. A quantity of hydrogen and water vapor standing over water in a measuring tube has a volume of 45.3 cc. The temperature is 22° C.; the barometer reads 738 mm. Correct the volume of hydrogen to standard conditions.

3. Ten liters of gas stand over water at 20° C. with the barometer reading 75 cm. The gas is passed through a drying agent and collected over mercury. If the temperature and barometric pressure remain constant, what will be its volume?

49. Kinetic theory of gases. It is really a surprising fact that the volume of all gases should be equally affected by changes of pressure and temperature. To explain the pressure exerted by gases it is now generally supposed that *all gases are made up of very minute particles called **molecules.*** These molecules are so minute that we cannot see them even with the most powerful microscope. In one cubic centimeter of a gas there are probably not less than 10^{19} (that is, 1 followed by nineteen ciphers) molecules. The spaces between the molecules are supposed to be much larger than the molecules themselves. This explains why gases are so easily compressed.

Then, too, it is conjectured that these little particles are flying about in all directions with great velocity and are traveling in straight lines, except when they hit each other and bounce off. The molecules of a gas seem to have no inherent tendency to stay in one place. This explains why gases diffuse so quickly and fill the whole interior of a containing vessel.

We may show the diffusion of bromine vapor by pouring a little liquid bromine into a cylinder. The red liquid quickly evaporates and diffuses up through the whole cylinder (Fig. 41).

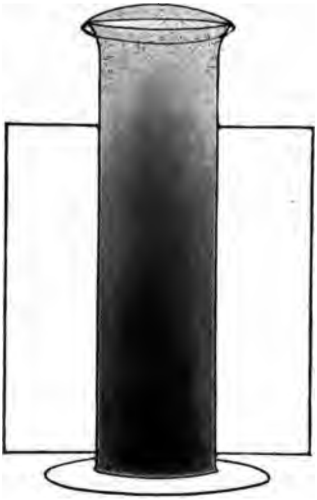


Fig. 41. Diffusion of bromine vapor upward.

The blows which the innumerable molecules of a gas strike against the surrounding walls constitute a continuous force tending to push out these walls. This accounts for gas pressures. When a gas is compressed to half its volume the pressure is doubled, because doubling the density doubles the number of blows struck per second against the walls. According to this theory the expansion of a gas when heated is due to the more rapid movement of its molecules and to their requiring, in consequence, more room in which to fly about.

In liquids we think of these molecules as being closely packed together; but in gases they are widely scattered with much vacant space between them. Thus a gas may be considered as a swarm of very minute particles. All laws of gases can be explained by this **kinetic molecular theory.**

SUMMARY OF CHAPTER V

DENSITY of a gas means the weight in grams of one liter of the gas under standard conditions.

STANDARD CONDITIONS are temperature 0° C. and pressure 760 mm. of mercury.

PRESSURE of a gas is made equal to atmospheric pressure by equalizing the water levels inside and outside the bottle.

BOYLE'S LAW: Volume of a gas at constant temperature varies inversely as pressure.

DENSITY of a gas varies directly as pressure.

LAW OF CHARLES: Volume of a gas under constant pressure varies as the absolute temperature.

ABSOLUTE TEMPERATURE scale begins 273° below centigrade zero.

GAS EQUATION: $\frac{PV}{T}=\frac{P'V'}{T'}$

To correct for water vapor **subtract aqueous tension from barometric pressure.**

A GAS **is supposed to be a** ***vacant space with minute particles scattered throughout.*** **These particles are called** ***molecules*** **and are supposed to be flying about in all directions with great velocity. Warming a gas causes more violent vibration of its molecules. Pressure of a gas is due to the blows which these molecules strike against the surrounding walls.**

QUESTIONS AND PROBLEMS

1. Why are gases so much more susceptible to changes in temperature and pressure than solids?

2. What advantages have 0° C. and 760 mm. as standard conditions over some other more common conditions?

3. When we say the pressure is 760 mm. what does that really mean?

4. What condition as to temperature must always be stated in Boyle's Law?

5. What condition as to pressure is assumed in stating the Law of Charles?

6. How would you actually go to work to weigh a gas?

7. If the water levels inside and outside the measuring vessel could not be conveniently equalized (Fig. 34 *B* and *C*), how would you make correction for this fact?

8. What do you suppose is the condition of the molecules at absolute zero?

9. If a gas is collected over mercury, do we need to make a correction for the pressure of the mercury vapor?

10. Why should you expect the pressure of water vapor to increase with the temperature?

11. What would be the aqueous tension at 100° C.?

12. It is an experimental fact that a gas, even if heavier than air, gradually leaves an open cylinder. How does the kinetic theory explain this?

13. The barometric pressure in the laboratory is generally less than 760 mm. Will the corrected volume be greater or less than the observed volume of a gas?

14. In collecting a gas over water the bottle is first filled with water and then inverted in a pneumatic trough. What keeps the water up in the bottle?

15. A certain quantity of oxygen measures 40 cc. when the pressure is 765 mm. and the temperature is 15° C. What will be its volume when the pressure is 740 mm. and the temperature is 25° C.?

16. Twenty cubic centimeters of hydrogen is contained in a measuring tube in which the level of the water is 39 mm. above the outside level; find the corrected pressure. Assume that the barometer stands at 740 mm., and the temperature is 21° C.

CHAPTER VI

WATER AND ITS COMPOSITION

Occurrence and importance — characteristic properties — change of state — solvent power of water — impurities in water — purification of drinking water.

Chemical composition of water — electrolysis — synthesis by volume — Gay-Lussac's Law of Volumes — synthesis by weight — percentage composition.

50. Occurrence and importance. Water is the most familiar of all chemical compounds. It covers about five-sevenths of the earth's surface and is present in varying amounts in many of the commonest objects. The soil under normal conditions contains water, which, as we all know, is necessary to the growth of plants. The plants themselves contain large quantities of it; in fact, most of the vegetables used for food are at least three-quarters water. The human body consists of about 70 per cent water, which is derived from our food and drink. The presence of water vapor in the atmosphere, its formation into rain and snow under varying conditions, and the important part it plays in climatic changes are familiar to everyone. Because water is fundamentally so important in the growth of plants and animals and in the production of climatic changes, it is not too much to say that life without it is impossible.

51. Characteristic properties. Pure water is an odorless liquid. In small quantities it is colorless, but large masses show a distinct blue color. When sufficiently cooled it solidifies to a colorless solid commonly known as ice; when heated it boils and changes rapidly into water vapor, or, as it is usually called, steam.

One cubic centimeter of water at 4° C. weighs 1 gram. Its **density** at 4° C. is, therefore, one gram per cubic centimeter.

The **specific gravity** of a substance is the ratio of its density to the density of water. Thus, the specific gravity of mercury is 13.6, which means that it is 13.6 times as heavy as water.

52. Changes of state. When liquid water freezes into ice or boils off as steam, we say that it has changed its state. All materials can be classified as **solid**, **liquid**, or **gaseous**. These are called the three states of matter. The transformation from one to another is a purely physical change, and the temperature at which it takes place is a very important physical property of the substance. The temperature at which water freezes to ice is taken as 0° on the centigrade thermometer and is marked 32° on the Fahrenheit scale. The centigrade scale is the one that is used in nearly all scientific work. The temperature at which solid ice melts to water is also 0° C. Liquid water is always passing to some extent into the gaseous state, a process which is called **evaporation**, familiar to everyone as the way in which wet clothes slowly dry. Since water vapor is a gas it is invisible, and the white clouds which are sometimes called steam are not gaseous water at all, but consist of very fine drops of water formed by the vapor as it suddenly returns to the liquid condition.

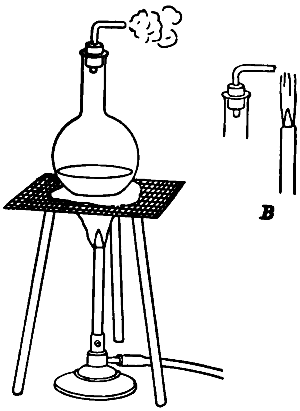


Fig. 42. Cloud of "steam" (*A*) disappears when heated (*B*).

We may demonstrate that gaseous water, or "live steam," is invisible by the following experiment: We place a little water in a large flask provided with a one-hole stopper and bent tube, as shown in figure 42 *A*. When the water boils rapidly a cloud of "steam" escapes from the tube. It will be seen that the flask is clear although full of steam. If we now hold under the jet of steam another Bunsen burner (Fig. 42 *B*), the cloud at once disappears because the flame has warmed the air so that the steam does not condense.

The evaporation of water at ordinary temperatures is slow but becomes more rapid as the temperature rises. When the temperature is raised sufficiently high, bubbles of water vapor rise through the liquid and the water is said to **boil.** At this point the evaporation is very rapid. The temperature at which this phenomenon takes place depends on the barometric pressure (Chapter V). The boiling point of water at 760 mm. pressure is 100° C. The temperatures at which a substance freezes and boils are called the **melting point** and the **boiling point** respectively.

53. Solvent power of water. Water will dissolve a great many substances; for example, salt and sugar. This process, in the simpler cases at least, is probably merely a mechanical one. We may consider the liquid which is formed by dissolving sugar in water (called a **solution**) as a mixture. We use water to make solutions of a great many different substances, both because water is cheap and easily obtained and because it will dissolve so many materials. We speak of the liquid which is used in making a solution as the **solvent**; we express the ease with which water dissolves substances by saying it has great solvent powers. (See Table of Solubilities in Appendix.) A water solution of a material is often called an **aqueous solution.**

54. Natural water is impure. Since water is such an excellent solvent it is never found pure. Sea water, for example, has a considerable amount of common salt and many other substances dissolved in it. Water obtained from certain wells and springs contains only a small amount of dissolved material; but the purest form of natural water is rain water. Even this, however, contains dust from the air and dissolved gases. Besides the dissolved impurities natural water usually has a great deal of material mechanically suspended in it. This generally consists of very fine particles of soil and causes what is commonly called "muddy water."

Still another sort of impurity is organic matter, which is partially suspended and partially dissolved and which consists of compounds formed from plants and animals. These come from the plant life in the soil and from sewage. Associated with the organic material and living on it are microörganisms, or bacteria, many of which cause disease. Their presence in water is almost always due to contamination with the waste products of animal life. Certain diseases, for example typhoid fever, are often contracted by drinking water which is thus polluted and into which the typhoid bacteria have found their way from persons suffering with the disease. Because water contaminated with sewage is very dangerous, towns and cities must go to extreme measures to obtain their supply from uncontaminated sources, and, if this is impossible, to purify carefully the water which is used.

55. Purification of water. *Water may be purified in four ways.* Only the first produces really pure water. The other methods remove or destroy some of the materials which make it unfit for drinking purposes.

(1) **Distillation.** All the dissolved and suspended materials can be removed by a process called **distillation.** The water is boiled in a vessel which is so arranged that the steam will pass through a cold tube and again return to the liquid condition (Fig. 43). This change of water vapor to liquid water is called condensation, and the apparatus in which it takes place is called a **condenser.** The water which drops from the end of the condenser is pure, the impurities being left behind in the *vessel in which* the water was boiled. Distilled

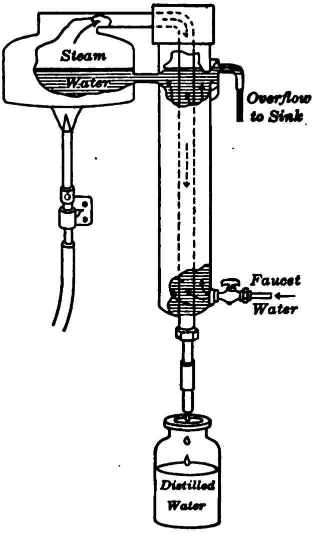


Fig. 43. Making distilled water in the laboratory.

water, as it is called, is used in the laboratory when pure water is desired. It is sometimes used for drinking purposes but has a peculiar " flat " taste because it contains no dissolved air or other materials. This taste may be partially removed by bubbling air through the water, which dissolves a small quantity of the air and thus becomes more palatable.

(2) **Filtration.** The suspended material in water may be removed by filtration. This is done on a large scale in cities where the only supply comes from muddy rivers, or similar sources. The water is allowed to pass slowly through beds of gravel and sand (Fig. 44). The suspended material is caught between the small particles of the sand and retained. The water issuing from the bottom of the filter bed still contains all the *dissolved* impurities, but it is free from suspended matter and is much more suitable for household uses.

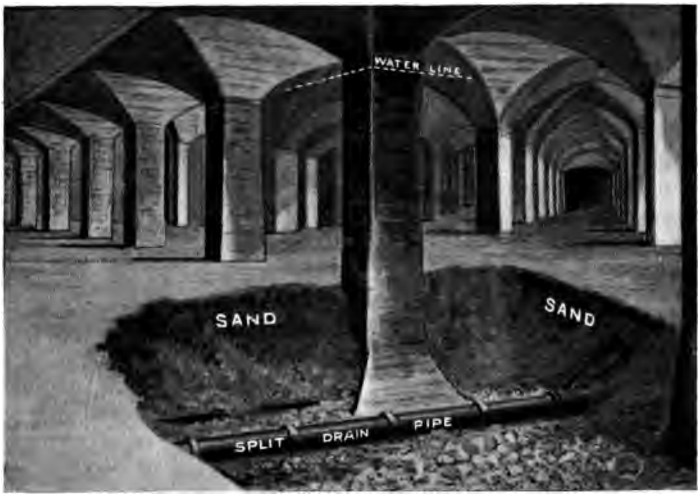


Fig. 44. Filtering water through beds of sand.

(3) **Boiling.** Water which contains harmful bacteria may be made fit to drink by boiling for a short while. This so-

called process of purification does not really remove any of the impurities, but merely kills the microörganisms (Fig. 45) which cause disease. These minute forms of plant life cannot live at the temperature of boiling water. When they are dead they can no longer cause disease. This method of treating water is very effective from the standpoint of health, but is too expensive to be utilized except on a small scale in special emergencies.

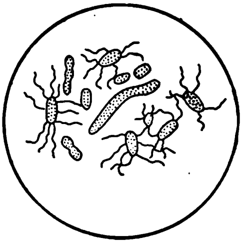


Fig. 45. Bacteria sometimes found in drinking water. (Greatly magnified.)

(4) **Chemical treatment of drinking water.** The bacteria may be destroyed by other methods besides boiling. A number of chemical substances when added to water in very small amounts kill the microörganisms. Chlorine and hypochlorous acid are two such materials; but we shall reserve a full discussion of this method of purification until we have considered these substances. This process of chemical purification is rapidly becoming very important. A process closely akin to it is the way in which natural running water will in time purify itself. The oxygen of the atmosphere dissolves in the water and chemically acts on the bacteria, destroying them. This is a slow process, but in a modified form has been used to some extent for purifying city water. The water is sprayed into the air in fountains, thus allowing as much opportunity as possible for the chemical action of the air.

Composition of Water

56. Decomposition of water. We have already seen (§ 9) that water may be decomposed by an electric current into hydrogen and oxygen. This chemical change can be represented thus:

$$\text{water} \longrightarrow \text{hydrogen} + \text{oxygen}$$

Besides this fact we *recall that* the volume of hydrogen generated

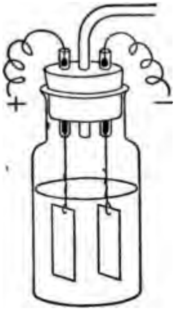


Fig. 46. A mixture of hydrogen and oxygen prepared by electrolysis.

was double that of the oxygen. Knowing the densities of hydrogen and oxygen we might compute the *weights* of these gases, which are the constituent elements in water, and so get the percentage composition of water.

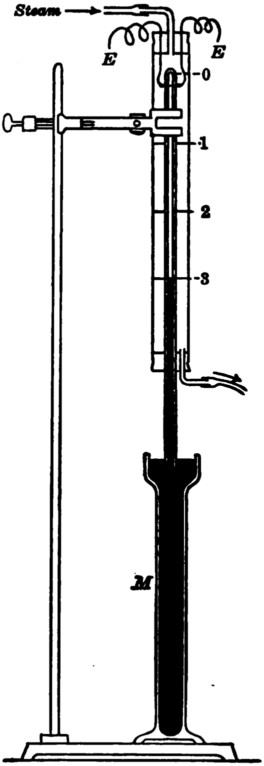


Fig. 48. Volume of steam produced by union of hydrogen and oxygen.

57. Synthesis of water by volume. The electrolysis of water is a method of decomposition, or analysis, which means "tearing apart." A more decisive determination of the composition of water is brought about by an actual observation of the fact that the gases hydrogen and oxygen unite in the proportion of two volumes of hydrogen to one of oxygen to form water. This process of experimentation is called synthesis, which means "putting together."

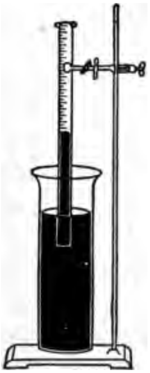


Fig. 47. Eudiometer tube containing a mixture of hydrogen and oxygen.

The experiment of combining the two gases is usually carried on in a piece of apparatus called a **eudiometer.** This is a graduated glass tube with two platinum wires fused through the glass near the closed end. There is a spark gap of 2 or 3 mm. between the ends of the wires. The tube is first entirely filled with mercury and inverted in a jar of the same liquid. Then a mixture of one volume of oxygen and two volumes of hydrogen is prepared by electrolysis (Fig. 46) and introduced into the tube (Fig. 47) until it is about three-fourths full of gas. An electric spark from an induction coil causes the gases to combine, and at once we see that the mercury rises until it reaches the top of the tube. The water formed has condensed to a slight dew.

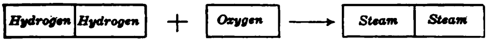
If the experiment is performed with the tube surrounded by a wider one through which steam passes (Fig. 48), the condensation of the resulting steam is prevented. In this case it is found that, when all the gases are measured at the same temperature (about 100° C.) and at the same pressure, *a shrinkage of one-third has occurred.* (Care must be taken to adjust the apparatus so that the top of the mercury in the tube, both before and after the change, is at the same height above the free surface of the mercury in the jar.)

FIG. 49. JOSEPH LOUIS GAY-LUSSAC (1778–1850).

A French chemist noted for his researches on the combining volumes of gases.

This experiment shows that the volume of the steam is just equal to the volume of the hydrogen. In other words,

2 vol. hydrogen + 1 vol. oxygen ⟶ 2 vol. steam.



58. Gay-Lussac's law of volumes. It is astonishing that the combining volumes of these gases should bear this simple and exact ratio to one another. When other gases are carefully studied in the same way, it is found that the ***volumes of gases used and produced in a chemical change can always be represented by the ratio of small whole numbers.*** This exceedingly interesting fact was discovered by Gay-Lussac (Fig. 49) in 1808.

59. Composition of water by weight. To determine the relative *weights* of the elements which are combined in water, we take advantage of the reaction between hydrogen and copper oxide. In this experiment we weigh the water produced by reducing a known weight of copper oxide. The loss in weight of the copper oxide gives us the weight of the oxygen used, and the difference between the weight of the water formed and the weight of the oxygen gives the weight of the hydrogen. The apparatus is essentially the same as that already shown in figure 31. The copper oxide (*A* in Fig. 50) is reduced; the water is collected and weighed in a U-tube (*B*) containing a drying agent, such as calcium chloride.

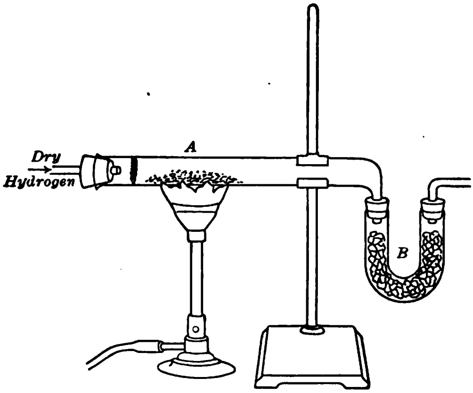


Fig. 50. Apparatus for finding the relative weights of hydrogen and oxygen in water.

This method of determining the composition of water was first used in 1820 by Berzelius, and the work was repeated in 1843 by Dumas. In recent years the American chemist Morley has determined the composition of water with very great precision. According to the results of his experiments, *1 part by weight of hydrogen combines with 7.94 parts by weight of oxygen to form water.* This is often called the **gravimetric synthesis** of water.

Such an experiment in which the weights or volumes of the materials involved are carefully measured is called a **quantitative** experiment. The other sort of experiment in which we observe only the nature of the change and the properties of the products is called a **qualitative** experiment.

60. Percentage composition of water. This experiment illustrates very well the Law of Definite Proportions; for it is found that all samples of pure water, from whatever source, show when analyzed that 1 part by weight of hydrogen has combined with 7.94 parts by weight of oxygen. From the fact that there is no change of weight during a chemical change (Law of Conservation of Matter) we know that the hydrogen must be $\frac{1}{1+7.94}$ or 11.2 per cent of water, and that the oxygen must be $\frac{7.94}{1+7.94}$ or 88.8 per cent of water. In other words, *water is about* $\frac{8}{9}$ *oxygen and* $\frac{1}{9}$ *hydrogen by weight.*

SUMMARY OF CHAPTER VI

WATER is one of the most *important compounds*.

Water exists in *three states:* solid (ice), liquid, and gaseous (steam). It freezes at 0° C. and boils at 100° C. One cubic centimeter of water at 4° C. weighs 1 gram.

Water is an excellent *solvent* for many substances; resulting solutions are called *aqueous solutions*.

NATURAL WATERS are impure; they contain dissolved and suspended material and sometimes bacteria.

PURE WATER can be prepared by *distillation*. Suspended material may be removed by *filtration*. Disease bacteria may be destroyed by boiling, or by adding small amounts of certain chemicals.

THE COMPOSITION of water can be shown by *analysis* and by *synthesis*. Two volumes of hydrogen unite with 1 volume of oxygen to form 2 volumes of steam.

LAW OF GAY-LUSSAC: The volumes of gases used and produced in a chemical change can always be represented by the ratio of small whole numbers.

COMPOSITION OF WATER BY WEIGHT: 1 part by weight of hydrogen and 7.94 parts by weight of oxygen.

QUESTIONS AND PROBLEMS

1. How would you prove that a certain colorless liquid was water?

2. How would you proceed to determine the total amount of solids present in a sample of water?

3. Why is rain water the purest form of natural water?

4. How could a steamship in mid-ocean obtain a supply of drinking water?

5. Can water be purified by freezing?

6. How would you destroy bacteria in water?

7. How could you prove that the air of the laboratory contains water vapor?

8. How could you demonstrate that "live steam" is colorless?

9. Name two or more other substances besides water which exist in three states.

10. Name two other common solvents besides water.

11. Why do we need to drink water?

12. If one liter of hydrogen under standard conditions weighs 0.09 grams, and one liter of oxygen under the same conditions weighs 1.43 grams, calculate from the results of the electrolysis of water its composition by weight.

13. When 20 cc. of hydrogen and 8 cc. of oxygen are placed in a eudiometer and ignited, what volume of steam is formed? What gas and how much of it remain in excess?

14. In studying the composition of water by weight Dumas obtained the following results:

Weight of water formed	945.439 g.
Oxygen taken from copper oxide	840.161 g.
Weight of hydrogen in water	105.278 g.

Compute the percentage composition of water from these figures.

15. A current of steam is passed over some clean iron filings which weigh 4.131 g. The iron filings are found to have increased in weight to 4.846 g. (*a*) What weight of steam has been decomposed in this experiment? (*b*) What weight of hydrogen has been set free? (*c*) What volume would it occupy under standard conditions?

(Assume 1 liter of hydrogen weighs 0.09 grams.)

REVIEW QUESTIONS

1. Write a careful statement of five *laws* which we have studied thus far.

2. Describe a laboratory experiment to illustrate each of these laws.

3. Write out a definition of each of these technical terms as used in chemistry: *element, substance, mixture, compound, alloy, catalyst, solvent, boiling point, melting point, absolute zero.*

4. Give an illustration of the correct use of each of the terms mentioned in number 3.

5. Describe two methods of showing experimentally that water contains hydrogen and oxygen, and explain the tests which must be applied in each case.

TOPICS FOR FURTHER STUDY

Drinking water. What is the source of your water supply? What methods of purification are used? Make a trip to the local water works. Is the appearance of water a safe indication of its desirability for drinking purposes?

Importance of water to life. What is the rôle of water in climatic changes? Is the prosperity of a country affected by the rainfall? What has been done in recent years to supply water to arid regions? How do you account for the presence of so much dissolved material in the sea, and so little in rivers, ponds, and most lakes?

CHAPTER VII

THE TWO OXIDES OF CARBON

Dioxide — production by burning and decay — test — used by plants — preparation by action of acids on carbonates — experiments — properties — liquid and solid — commercial uses.

Monoxide — produced in coal fire — by reduction — from formic acid — properties — uses.

Composition of the dioxide and monoxide — LAW OF MULTIPLE PROPORTIONS.

61. Production of carbon dioxide. When we burned charcoal (carbon) in oxygen (§ 19), the product was a gas which we called carbon dioxide. This process is going on all about us wherever charcoal, coke, coal, or wood — fuels which are largely composed of carbon — are being burned. This same gas is being produced on an even greater scale by the slow combustion of food in animals, and by the decay of wood and dead leaves.

One of the essentials of the life process in animals is the slow oxidation of the food which has been consumed; this oxidation liberates the heat which keeps the body warm. The oxidation takes place by means of the oxygen of the air which is breathed. The products of the combustion — carbon dioxide and water vapor — are exhaled with each breath.

We may prove that carbon dioxide is present in the breath by a simple experiment. If by means of a glass tube we blow through some clear limewater* in a large test tube, as shown in figure 51, we notice that at first the breath bubbles produce practically no change; but as soon as the breath comes from farther within the lungs, the clear liquid quickly becomes milky, showing the presence of carbon dioxide. *The production of milkiness in limewater is a characteristic of carbon dioxide.*

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* To make limewater, place a handful of powdered lime in a big bottle and fill this up with water; cork it up, and shake it for a minute. Then leave the mixture overnight to settle and pour off the clear solution for use.

To demonstrate the fact that carbon dioxide is produced when any carbon compound is burned in the air, we may set fire to a piece of paper and drop it while burning into a dry bottle. We then pour in a little limewater, cover the bottle with a glass plate, and shake it up.

We may also hold a dry bottle inverted over a candle flame and show the presence of carbon dioxide by means of limewater.

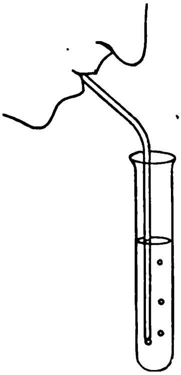

Fig. 51. Blowing through limewater to show the presence of carbon dioxide in the breath.

62. How plants use carbon dioxide. At first thought it would seem that the constant production of this great amount of carbon dioxide must fill the atmosphere with the gas. The fact is, however, that when pure air in the country is analyzed, it is never found to contain more than three or four hundredths of one per cent of it. This is because most plants reverse the process which takes place in animals; they absorb carbon dioxide from the air and give off oxygen.

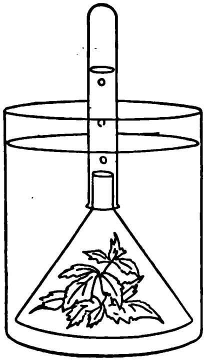

Fig. 52. Green leaves give off oxygen.

The liberation of the oxygen can easily be shown by placing a green plant under water in a jar, as in figure 52, and then setting the jar in the sunlight. Bubbles of gas appear on the leaves, grow larger, and then detach themselves and rise to the top. This gas may be collected in a test tube and tested with a glowing splinter of wood. *It is oxygen.*

We shall see in the next chapter that the small amount of carbon dioxide in the air varies very little; it is of the greatest significance because of the intimate relation it bears to the life of all plants and animals.

63. Preparation of pure carbon dioxide. It is possible to prepare pure carbon dioxide by burning carbon in oxygen, but it is difficult to separate the gas from the unused oxygen. In the laboratory it is usually prepared by the action of an acid on marble, which is a chemical compound called calcium carbonate made up of the elements calcium, carbon, and oxygen. When a dilute acid, such as hydrochloric acid, is brought into contact with a carbonate, a vigorous **effervescence**, or bubbling, takes place and continues until either the marble or the acid is all used up. This effervescence somewhat resembles boiling, except that the vapor which rises in **boiling** is always the same substance as the liquid from which it comes.

To collect the gas evolved in this chemical action we may use the same apparatus as in preparing hydrogen (Fig. 24). Pieces of marble are placed in the bottle and dilute hydrochloric acid is poured in through the thistle tube. The action starts at once and the gas may be collected as usual in bottles in the pneumatic trough.

64. Experiments with carbon dioxide. To study the properties of this gas we may perform the following experiments:

(1) A lighted taper is inserted into a bottle of the gas. The flame is at once put out.

(2) We dip a stirring rod into some limewater and then withdraw it so that a clear drop hangs from its end. If this is lowered into a bottle of the gas it immediately becomes clouded, or milky, in appearance. This is a **test for carbon dioxide.**

(3) We may lower a short piece of lighted candle into a wide-mouthed beaker and then pour the gas from one of the bottles over the candle. The candle goes out, which shows that this gas is heavier than air.

(4) Let us color some water with a few drops of a dye solution known as **litmus**, and let gas from the generator bubble through it for a few minutes. It will be noticed very soon that the *litmus has turned red, which is a proof of the presence of an acid.* This gas dissolves to a small extent in water, and the resulting solution, as we have seen, is an acid. For this reason the gas is often called in commerce "**carbonic acid gas.**"

65. Properties of carbon dioxide. In our experimental study we find that carbon dioxide is a gas without color or odor. Since it is a little more than one and one-half times as heavy as air, it can be poured from one vessel into another almost like water (Fig. 53). It is somewhat soluble in water. As with all gases its solubility is greatly increased by increase in pressure and, conversely, becomes less with diminished pressure. This fact is taken advantage of in so-called **carbonated water**, and in many beverages, such as ginger ale. The beverage is treated with carbon dioxide under pressure and dissolves considerable quantities of the gas. The bottle containing the liquid is closed while still under pressure. When the cork is removed the gas escapes and produces the familiar effervescence (Fig. 54).

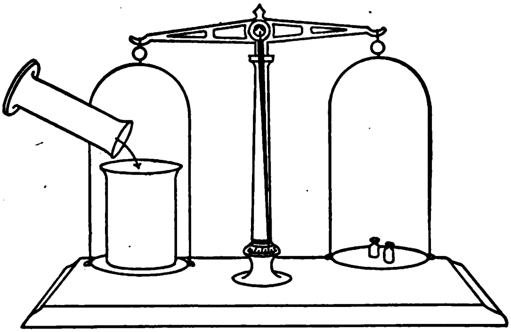
Fig. 53. Scale pan weighed down by carbon dioxide.

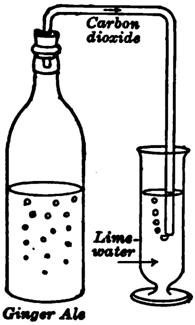

Fig. 54. Carbon dioxide evolved from ginger ale causes a precipitate in lime-water.

The most characteristic chemical property of carbon dioxide is its inertness. It will neither burn nor support combustion. It readily combines with one class of substances called **alkalies**, forming a group of compounds named the carbonates. Lime is an alkali which is chemically known as calcium hydroxide, and the white precipitate which is formed when lime-water and carbon dioxide react is calcium carbonate. This calcium carbonate is exactly the same chemical compound as ordinary marble, and is called "precipitated chalk."

66. Liquid and solid carbon dioxide. By applying sufficient pressure to carbon dioxide gas at ordinary temperatures it may be condensed to a liquid. This liquid is an article of commerce and is put on the market in strong steel tanks. When the liquid carbon dioxide runs from such a tank, part of it evaporates quickly and removes so much heat that the rest is frozen to a snow-like solid.

A tank of carbon dioxide is tilted on its side, as shown in figure 55. A stout flannel bag is tied around the outlet and the valve is opened wide. After a few minutes the bag is found to contain a snow-like solid. This solid has very fascinating properties. It quickly disappears when left by itself, as it rapidly changes into gas. A portion of it placed on water very soon evaporates, but in so doing it removes heat from the water and freezes the latter.

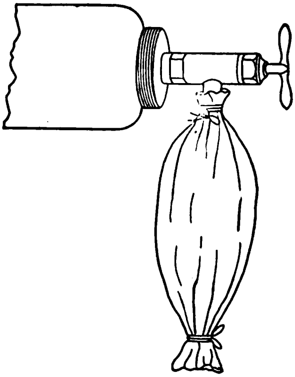

Fig. 55. Liquid carbon dioxide boiling and freezing.

If the solid is put in a beaker and mixed with ether, the mixture will freeze a test tube of mercury. The ether serves to carry the heat quickly from the test tube to the solid.

Caution. In handling the solid carbon dioxide one must avoid pressing it against the flesh, otherwise it causes a frost bite which feels very much like a burn.

Solid carbon dioxide enables us easily to reach a temperature as low as −40° C. It is sometimes used for refrigeration purposes.

67. Commercial uses. Carbon dioxide has a number of important uses. We have already mentioned its extensive use in the preparation of carbonated beverages. The **soda water** of the drug store, which was originally prepared by mixing baking soda in solution with some fruit acid, is now made by connecting a tank of the gas with a supply of water, in such a way that a solution of carbon dioxide issues when the faucet is opened. Many **fire extinguishers** (Fig. 56) depend on carbon dioxide for their effectiveness. The body of the container is filled with the water solution of a carbonate, generally sodium bicarbonate. A small bottle at the top contains sulfuric acid. When the extinguisher is turned upside down, the acid comes in contact with the carbonate and produces carbon dioxide. The gas thus produced forces the liquid out through the hose and also comes out itself. Since carbon dioxide is heavy and noninflammable, it partially excludes the oxygen of the air and assists the water in putting out the fire. Such extinguishers are very effective but somewhat heavy to handle.

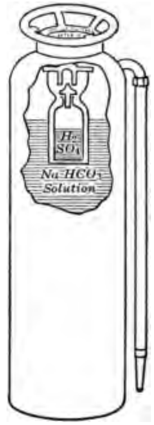

Fig. 56. Carbon dioxide fire extinguisher.

CARBON MONOXIDE

68. Formation in a coal fire. When carbon or a substance containing carbon burns in a *limited* supply of air or oxygen, carbon monoxide is formed. This gas is an oxide of carbon containing less oxygen than carbon dioxide and having quite different properties. It burns in the air with a characteristic blue flame, forming carbon dioxide. The burning of a coal fire in a range offers an interesting example of this (Fig. 57). The hot coal on the grate coming in contact with the oxygen of the entering air burns to carbon dioxide. But this gas on passing through the upper layer of coal, where the supply of air is restricted, is reduced to *carbon monoxide.* *At the top* of the glowing layer of coal, where

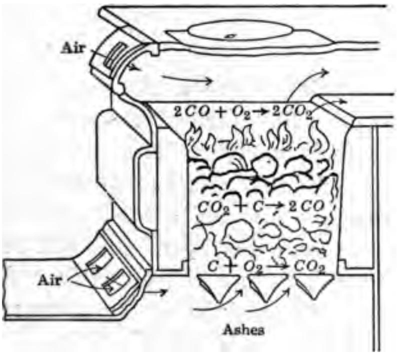
Air
$2CO + O_2 \rightarrow 2CO_2$
$CO_2 + C \rightarrow 2CO$
$C + O_2 \rightarrow CO_2$
Air
Ashes

Fig. 57. Formation of the oxides of carbon in a coal fire.

abundance of air can find access, the carbon monoxide again burns to carbon dioxide with the well-known blue flame. This carbon monoxide is commonly called "**coal gas**" and is familiar to everyone who has used anthracite (hard) coal.

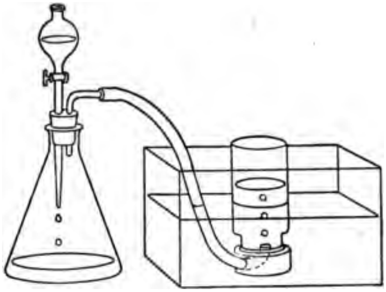

Fig. 58. Preparation of carbon monoxide by action of warm sulfuric acid on formic acid.

69. Laboratory method of preparation. We can prepare carbon monoxide by passing carbon dioxide through a tube containing charcoal. The charcoal must be heated red-hot, and the issuing gas must be passed through a solution of caustic soda in order to absorb any of the carbon dioxide which remains undecomposed. The residual gas, carbon monoxide, may be collected over water.

An easier method is to treat formic acid with warm concentrated sulfuric acid. The latter causes the decomposition of the formic acid into water and carbon monoxide. The apparatus may be set up as shown in figure 58.

70. Properties of carbon monoxide. Carbon monoxide is a colorless gas, nearly odorless, just a little lighter than air, and very slightly soluble in water. It is one of the gases which it is difficult to liquefy. Its most striking chemical property is the fact that it *burns in air or oxygen with a blue flame, forming carbon dioxide.* It also acts as a **reducing agent** and will reduce metallic oxides, such as copper oxide or iron oxide. In Chapter XXXI we shall see that the ores of iron are commercially reduced by this gas in a blast furnace.

The reducing action of carbon monoxide may be very well shown by the following experiment. The gas is prepared in the flask *A* (Fig. 59). The bottle *B* contains a little water to wash the gas, and the hard-glass tube *C* holds the black copper oxide which is heated. The metallic oxide is reduced by the gas to reddish metallic copper, and the carbon monoxide is oxidized to carbon dioxide. The presence of this latter gas is shown by the milkiness produced in the limewater in bottle *D*. Any of the unchanged carbon monoxide which passes through is collected over water in *E* and then burned.

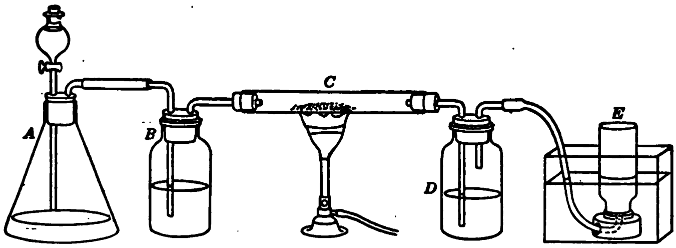

Fig. 59. Copper oxide reduced by carbon monoxide.

The results of this experiment can be briefly stated thus:

$$\underset{\left[\begin{smallmatrix}\text{copper}\\ \text{oxygen}\end{smallmatrix}\right]}{\text{copper oxide}} + \underset{\left[\begin{smallmatrix}\text{carbon}\\ \text{oxygen}\end{smallmatrix}\right]}{\text{carbon monoxide}} \longrightarrow \text{copper} + \underset{\left[\begin{smallmatrix}\text{carbon}\\ \text{oxygen}\end{smallmatrix}\right]}{\text{carbon dioxide}}$$

Carbon monoxide is extremely poisonous. Less than half of one per cent of this gas in the air causes a severe headache, and large amounts may cause death. Every winter there are cases of men who are poisoned while working about an automobile in a small closed garage. The exhaust gases of the gasolene engine contain some carbon monoxide. Sometimes the gas escapes into the room from a coal stove when the draft is not properly regulated; cases of sickness and even of death have resulted from this cause. Illuminating gas, especially that known as water gas, contains carbon monoxide, which is particularly dangerous, since it is itself practically odorless and cannot be recognized in the air. Fortunately illuminating gas generally contains some other substance which has a pronounced smell and thus gives warning of the presence of the poisonous material. In mine explosions carbon monoxide is always formed; and since birds are very sensitive to this poison, the rescuers often carry canaries with them to warn them of their own danger. In recent years oxygen helmets (Fig. 60) have been provided for miners to use in such emergencies.

Carbon monoxide is poisonous because it combines with the red corpuscles of the blood and prevents them from taking up oxygen from the air. Since the life of a person depends on the absorption of oxygen by these blood corpuscles, carbon monoxide causes a sort of internal suffocation, which results in sickness and sometimes death.

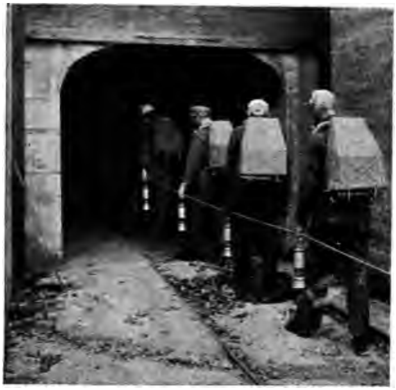

Fig. 60. Miners use oxygen helmets in the presence of carbon monoxide.

71. Composition of carbon dioxide and carbon monoxide. The weights of carbon and oxygen which combine to form carbon dioxide have been determined with great precision. The results of a great number of experiments have shown that the ratio of the weight of carbon to that of oxygen is as 1 : 2.66.

Carbon monoxide has also been very carefully investigated, and it has been found that the ratio of the weight of carbon to that of oxygen is as 1 : 1.33. It will be seen that 2.66 is exactly twice 1.33; that is, the weight of the oxygen combined with the carbon in carbon dioxide is exactly *twice* the amount combined with the carbon in the monoxide. This is a strikingly simple relationship, and is indicated by the names **di**(two)oxide and **mon**(one)oxide.

72. Law of multiple proportions. The case of carbon monoxide and dioxide is not peculiar. It has been found that, whenever there are two or more compounds containing the same elements, the weights of the one element which are combined *with a fixed* weight of the other always bear a simple relationship to each other, such as 2 to 1, or 3 to 1, or 3 to 2. This generalization is known as the LAW OF MULTIPLE PROPORTIONS and was first stated by John Dalton in 1804. It may be conveniently expressed in somewhat different language as follows: *When any two elements A and B combine to form more than one compound, the weights of B which unite with a fixed weight of A are in the ratio of small whole numbers.*

This law together with the Law of Definite Proportions is the foundation of chemistry. In a later chapter we shall see how Dalton explained these simple generalizations by means of a theory which has made the science of chemistry possible.

SUMMARY OF CHAPTER VII

CARBON DIOXIDE is formed when carbon or carbon compounds burn or decay.

It can be *prepared:*

(1) by burning charcoal in air or oxygen;

(2) by the action of acids on carbonates.

Its *properties:* a colorless gas, slightly soluble in water, and suffocating but not poisonous. It is about 1.5 times as heavy as air. Easily liquefied. Evaporating the liquid produces solid carbon dioxide.

TEST: Does not burn; combines with alkalies and *produces a milkiness in limewater.*

USED in making carbonated beverages such as soda water; in certain types of fire extinguishers; and in ice machines.

CARBON MONOXIDE is formed:

(1) when carbon or carbon compounds burn in a limited supply of air;

(2) by the reduction of the dioxide;

(3) by action of warm sulfuric acid on formic acid.

Its *properties:* a colorless gas and practically odorless, slightly lighter than air, and insoluble in water. Very poisonous. Burns with a blue flame, forming the dioxide. Acts as a reducing agent, *taking oxygen from hot metallic* oxides, such as copper and iron.

COMPOSITION OF THE OXIDES OF CARBON: Weights of carbon to oxygen

in the dioxide are as 1 : 2.66;

in the monoxide are as 1 : 1.33.

LAW OF MULTIPLE PROPORTIONS: When any two elements *A* and *B* combine to form more than one compound, the weights of *B* which unite with a fixed weight of *A* are in the ratio of small whole numbers.

QUESTIONS

1. How could you distinguish between carbon monoxide and carbon dioxide?

2. How could you distinguish between carbon monoxide and hydrogen?

3. When alcohol burns, carbon dioxide is formed. What does this show about the composition of alcohol?

4. Does the fact that an acid produces effervescence when added to a material prove the presence of carbon dioxide?

5. How would you test for a carbonate?

6. A beaker of limewater is left standing in the laboratory overnight. The next day the liquid is covered with a white material. Explain.

7. Name two important reducing agents which we have studied thus far.

8. Two samples of illuminating gas contain 6% and 33% of carbon monoxide respectively. Which is the more poisonous?

9. Upon what three properties of carbon dioxide does its use in fire extinguishers depend?

10. How is the quantity of carbon dioxide in the atmosphere kept nearly constant?

11. When the stopper is removed from a bottle of mineral water, it effervesces. How could you prove the bubbles to be carbon dioxide?

12. When carbon dioxide is passed over hot powdered zinc, zinc oxide is formed. What is the other product?

13. The so-called "water gas" is mainly a mixture of hydrogen and carbon monoxide. Why is water gas better for heating than for *illuminating?*

14. What effect would doubling the pressure have upon the solubility of carbon dioxide in water?

15. Carbon dioxide is sometimes spoken of as plant food. Explain.

16. Tobacco smoke is said to contain some carbon monoxide produced by incomplete combustion. How may a smoker avoid this poison?

TOPICS FOR FURTHER STUDY

Heating apparatus in the home. Investigate your kitchen stove. Draw a diagram of it, and indicate what chemical reactions take place at each point. How is your house heated? Make a sketch of the system. Is there any danger of carbon monoxide escaping into the rooms? What might happen if the lining of the fire box in a hot-air furnace was defective?

Coal-mine explosions. What is the cause of explosions and fires in coal mines? What steps have been taken by the mining companies and the government to reduce the danger from this source? (Consult pamphlets issued by the Bureau of Mines.)

CHAPTER VIII

NITROGEN AND THE ATMOSPHERE

Importance of nitrogen — preparation from air and by decomposition of compounds — properties. Air, a mixture — liquefaction — commercial uses of nitrogen. Rare gases in air — use of helium. Composition of air — rôle of carbon dioxide in nature — impurities in "bad air" — fresh air.

73. Importance of nitrogen. We have already learned (§ 22) that about one-fifth of the air is oxygen; nearly all the remainder is the elementary gas called nitrogen. Combined with other elements it is present to a limited extent in certain mineral deposits, such as saltpeter. Compounds containing nitrogen are *essential* to life, and are present in all living matter and in its decomposition products. In fact, a valuable constituent of our food is protein material, which contains a large percentage of chemically combined nitrogen. Soils and fertilizers serve as food for plants very largely in proportion to the percentage of nitrogen which they contain. The compounds of nitrogen are so important that we shall consider them in separate chapters (XIX, XX), confining our attention at present to the element itself and to the air.

74. Preparation from air. As has been said, Lavoisier found that air contains oxygen, which may be removed by causing it to combine with mercury. We can, however, remove the oxygen much more quickly by burning phosphorus, and can thus obtain fairly pure nitrogen.

We place a piece of phosphorus (wiped dry) in a porcelain crucible *which rests on a cork floating* on the surface of a pan of water. It is ignited with a hot wire, and a jar is placed over the burning solid, as shown in figure 61. The phosphorus burns in the confined air in the jar, and forms the same dense white smoke as when burned in pure oxygen. We then allow the jar to stand for a short time so that it may cool, and the fumes, which consist of very fine, solid particles of oxide of phosphorus, may dissolve in the water. It will be noticed that the *water has risen in the jar about one-fifth*, taking the place of the oxygen. If we now introduce a lighted taper or candle into the gas in the jar, we find that the flame is at once extinguished. The residual gas will not support combustion.

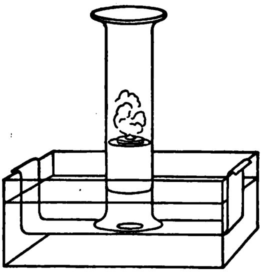

Fig. 61. Removing oxygen from air by burning phosphorus.

This inert gas was called by Lavoisier **azote**, which signifies that it is incapable of supporting life. Later it was named **nitrogen** because of its presence in saltpeter, or niter. Animals cannot live in nitrogen, not because it is in any way poisonous, but simply because animals *must* have free oxygen. They die of suffocation in nitrogen just as they drown in water.

75. Preparation of pure nitrogen. Until rather recently it was thought that pure nitrogen could be prepared from air by removing all the oxygen and the small amount of carbon dioxide that is always present. But it has been found that such nitrogen contains about one per cent of impurities, which are the so-called "rare gases."

Pure nitrogen can be most conveniently prepared in the laboratory by heating a compound of nitrogen called ammonium nitrite. This decomposes into nitrogen and water. Inasmuch as ammonium nitrite is unstable, we use a mixture of sodium nitrite and ammonium chloride. The reaction, however, is complicated, and we need not consider it at this point.

76. Properties. Nitrogen is like oxygen and hydrogen in having neither color, taste, nor odor; but in other respects it is very *different. For instance,* it does not burn and does not support combustion. In fact, its only characteristic which can be easily shown is that it does not readily enter into chemical reactions. It does, however, unite, although slowly, with certain other elements, provided these are heated to the proper temperature. It unites with red-hot magnesium, forming a compound of magnesium and nitrogen called **magnesium nitride.** When electric sparks are passed through a mixture of nitrogen and oxygen, the nitrogen will combine with oxygen to form **oxides of nitrogen.** In the presence of a suitable catalyst it will also combine with hydrogen at a moderately high temperature to form ammonia, which is a gaseous compound of nitrogen and hydrogen. Although these last two reactions take place only with difficulty, yet they have recently become of great importance because they enable us to transform the free nitrogen of the air into compounds of nitrogen. Compounds of nitrogen are essential to plant life, and their preparation from the nitrogen of the air is a modern chemical problem of enormous importance.

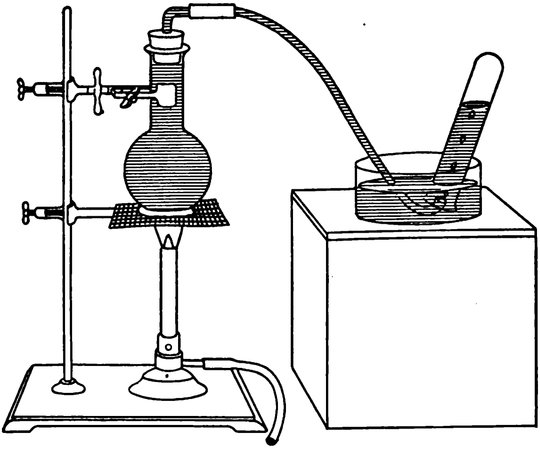

Fig. 62. Air expelled from water by boiling.

77. Air a mixture. The oxygen and nitrogen in air are not chemically combined. Air is only a mixture of these two gases and very small amounts of some others. There are a number of pieces of evidence which clearly show that *air is a mixture and not a chemical compound.*

(1) In the first place, pure nitrogen and oxygen can be mixed together to form an "artificial air" which is almost identical with ordinary air. There is no heat evolved or other sign of a chemical reaction when these gases are mixed. The proportions of the gases in this "artificial air" may be varied very considerably without appreciably affecting the chemical properties of the product. If the oxygen and nitrogen were chemically combined, there would be one definite proportion in which they would unite.

(2) In the second place, water will dissolve air; if we expel this air from the water by boiling (Fig. 62) and then analyze it, we find that it contains nearly twice as much oxygen as the original air. Oxygen is more soluble in water than nitrogen, and therefore relatively more of it dissolves. If the oxygen and nitrogen were combined, the dissolved gas would have the same composition as the air.

(3) Finally, we can separate air into its components by a purely physical process. This is done by liquefying the air and then carefully boiling off the more volatile nitrogen. If air were a compound, it would all boil at the same temperature.

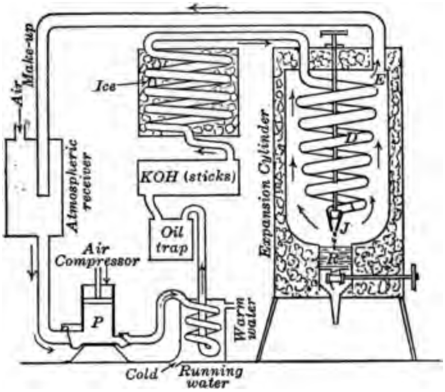

Fig. 63. Diagram of essential parts of liquid-air machine.

78. Liquefaction of air. There is a definite temperature below which a gas must be cooled before it can be liquefied (Chapter IV). This is known as the **critical temperature**, and is different for different gases. In the case of both oxygen and nitrogen the critical temperature is so low that it is impossible to liquefy these gases at ordinary temperatures, however much we compress them. To liquefy air *we must cool it to a very low temperature as well as subject it to a high pressure.* This is done on a large scale in an apparatus which is constructed as in figure 63.

This diagram shows only the essential parts of the apparatus. The air is compressed by a pump P, and the heat produced by the compression is removed by passing the air through cooling coils. The compressed air is made to expand rapidly by allowing it to issue from a very small jet J into an expansion cylinder kept at a lower pressure. As the air passes through this jet and expands, it absorbs a great deal of heat. *When a gas is compressed it gives out heat, and when a gas expands it absorbs heat.* This heat is removed from the gas, which is under pressure, by causing the expanded gas to flow back over the outside of the high-pressure pipe D through the cylinder. The cold expanded air is then compressed again and the process continued. Finally the gas is cooled so low by its own continued expansion that it liquefies and is collected in vessel R, from which it can be drawn off as needed.

Fig. 64. United States plant at Muscle Shoals, Ala., for producing liquid air and separating nitrogen.

We have just seen that *air*, like many other gases, *is liquefied by the combined effect of pressure and low temperature.* Liquid air is really only a mixture of liquid nitrogen (boiling point, −195.7° C.) and liquid oxygen (boiling point, −182.9° C.). It is commercially possible to separate the more volatile nitrogen from the oxygen. In this way oxygen is manufactured for industrial use and is compressed into steel tanks. Nitrogen is also prepared commercially (Fig. 64) by the same process, but to a limited extent.

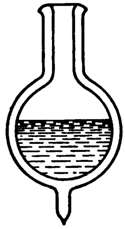
Fig. 65. Dewar flask.

79. Experiments with liquid air. Liquid air is coming to be a commercial article which can be purchased in many places. If poured into an ordinary glass vessel, it quickly absorbs enough heat through the glass to cause it to boil away completely. It can be kept or transported only in an especially constructed apparatus called a Dewar flask (Fig. 65). This flask consists of two glass vessels, one inside the other, the intermediate space being exhausted with a vacuum pump. The liquid air in such a flask is thus surrounded by a vacuum, which conducts heat very slowly, and consequently the liquid will not readily evaporate. To decrease the evaporation still further, the flasks are often silvered; this causes the heat to be reflected away from the exterior. The flask is also carefully packed in a basket with some nonconductor, such as felt, to prevent the inflow of heat from the outside. The well-known thermos bottle (Fig. 66) is constructed on the same plan and may be used to keep liquids either hot or cold for several hours.

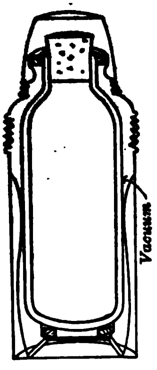

Fig. 66. Cross section of thermos bottle.

Ordinary materials manifest peculiar properties when cooled to the temperature of liquid air. For example, if a small rubber ball is immersed in liquid air and then dropped on the floor, it breaks into many pieces as if made of glass. In the same way a rubber tube which conducts liquid air soon becomes so brittle that it breaks to pieces. Flowers and grass are frozen solid by immersion in liquid air and are very brittle when removed. If a burning stick is plunged into liquid air it keeps on burning. A flame of hydrogen or coal gas dipped under the surface of liquid air goes on burning, and the water which is formed freezes.

80. Uses of nitrogen. Free nitrogen is used to fill certain kinds of electric-light bulbs. On account of its inertness it does not attack the white-hot filament in the lamp. When mercurial thermometers are to be used at temperatures from 300° to 500° C., the space above the mercury in the stem is filled with nitrogen under pressure. In this way the mercury is prevented from boiling, even at temperatures above its normal boiling point (357° C.). To a limited extent free nitrogen is used in the preparation of certain nitrogenous fertilizers (§ 243).

FIG. 67. SIR WILLIAM RAMSAY (1852–1916).
An English chemist who discovered the rare gases in the atmosphere.

81. Rare gases. Five elements — argon, neon, helium, krypton, and xenon — occur in the air in very small quantities. Argon, which is the most abundant of these, occurs to the extent of only 0.94 of one per cent by volume. The other four together constitute less than 0.002 per cent of the air. **Argon** was first discovered in 1894 by Sir William Ramsay (Fig. 67) and Lord Rayleigh; they removed all the oxygen and nitrogen from air by chemical methods, a very long and tedious process. It has since been found possible to prepare argon more conveniently by the liquefaction of the nitrogen and oxygen. Argon boils at a lower point than even oxygen, and can thus be separated from both nitrogen and oxygen by the liquefaction of the latter. The other elements are present in such minute amounts that their isolation and study was a matter of very long and painstaking research.

These five elements are all remarkably inert substances; it has not yet been found possible to make them enter into any chemical reaction. For this reason argon is sometimes used in the place of nitrogen for filling electric-light bulbs, being prepared commercially by the liquefaction of air.

82. A new use for helium. Helium has very recently come to be a substance of practical importance. Next to hydrogen it is the lightest known gas, being about seven times lighter than air. It is noninflammable and therefore an ideal substance for filling balloons and dirigibles; for most of the serious accidents which have occurred in the past have been due to the hydrogen's catching fire. Under the stress of the recent war the production of helium for aëronautical purposes has been accomplished on a large scale, and it is expected that the use of this gas will be of great importance in the future development of balloons and lighter-than-air airships. Certain natural gases which issue from the ground in some parts of the United States contain as much as 3 per cent of helium. By a process of liquefaction helium, which boils at the very low temperature of −269° C., can be separated from the other gases.

83. Composition of the air. Samples of air taken in the open country have all been found to have the same composition, except for the content of water vapor. The composition of a sample of dry air is as follows:

100 volumes of air contain

Nitrogen	78 volumes
Oxygen	21 volumes
Argon	0.94 volumes
Carbon dioxide	0.04 volumes
Helium, neon, krypton, xenon	traces

In cities and in poorly ventilated places the composition of the air may be very different. The changes in composition of the air which occur in such regions are, however, insignificant when compared with the large bulk of air which surrounds the earth. This great ocean of gas is constantly being stirred by the winds and air currents, and thus its composition, if taken in the open country, is always constant.

84. Carbon dioxide in the air. Although the amount of carbon dioxide in the air is usually very small indeed, it plays a most important rôle. This gas is pouring into the atmosphere from every chimney and smoke stack; it is produced wherever carbon compounds burn or decay; and is being exhaled by every living organism. On the other hand, all green plants absorb from the air carbon dioxide, which unites in the leaves with the water which has been absorbed from the soil by the roots. The products of this wonderful synthesis are starch and sugar (which are compounds of carbon, hydrogen, and oxygen), and oxygen, which is set free. We have seen (§ 62) the bubbles of oxygen rising from plants which were growing under water.

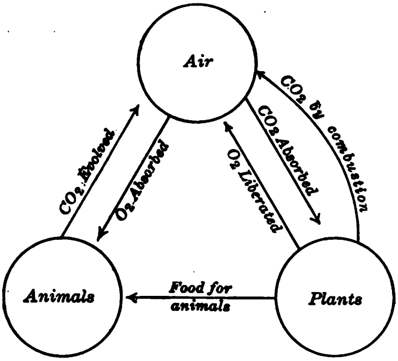

Fig. 68. Diagram to show the cycle of carbon and oxygen.

The chemical change which converts inorganic material (carbon dioxide and water) into living matter *can take place only in the sunlight,* and is brought about by the aid of the green coloring material in the leaves.

Thus it will be seen that animals and plants are complements of each other as regards the supply of oxygen and carbon dioxide in the air. The plants remove the carbon dioxide from the air and convert it into compounds, which in turn become food for the animals. The animals burn this food and exhale carbon dioxide (Fig. 68).

85. Impurities in the air affecting human comfort. We are all familiar with the so-called " bad air " which is found in overcrowded, poorly ventilated rooms, and the disagreeable feelings which this "bad air" produces. It was formerly thought that the chief factor in air which influenced human comfort was carbon dioxide, since the carbon dioxide content is always high in crowded, stuffy rooms and the oxygen content lower than normal. But this view has been shown to be erroneous. It is true that healthful air must contain a certain minimum of oxygen and that one can suffocate in an atmosphere containing too much carbon dioxide. Yet the amount of carbon dioxide which is found in even the worst ventilated rooms is far below this amount. *The chief factors which really determine whether or not air is pleasant to breathe are:* (1) **moisture**, (2) **temperature**, (3) **dust**, (4) **minute amounts of complex compounds exhaled by men and animals.**

The first two factors are closely associated. The human body is normally at a constant temperature of 98.6° F. (37° C.), and this temperature is regulated by the evaporation of water from the surface of the body. If the surrounding atmosphere is particularly moist, this evaporation proceeds with difficulty, and the regulation of the body temperature is correspondingly difficult. Very hot, moist air is one of the most disagreeable atmospheres in which to work. Similarly, if the air is too dry the evaporation from the body proceeds too rapidly, and the normal physiological activities are upset. A proper regulation of the moisture content (called **humidity**) is one of the essentials for comfort. Another important factor is, of course, the proper regulation of the **temperature**.

The presence of **dust** in the air causes a great deal of discomfort. Air in cities and in crowded rooms contains large amounts of dust, which not only irritates the respiratory organs but contains disease-producing bacteria. Air in the country after a good rain is relatively free from dust, and is always more pleasant to breathe than the dusty air of the city street after a long period of drought.

The fourth factor which affects air is noticeable only in poorly ventilated rooms containing many people. The human body gives off very small amounts of substances which cause the air to have a disagreeable physiological effect. These minute impurities probably affect people by their disagreeable odor and possibly also because they are actually poisonous to the human system. Whatever the reason, they cause the air of a crowded room to produce drowsiness, general discomfort, and even severe headaches.

The impurities and the dust may be removed from the air by washing it with a sort of shower bath of water. Very successful systems of ventilation have been installed in which the air is drawn out of the rooms, passed through a washer, partially dried, and sent back into the rooms again. Although the carbon dioxide content in such air may be relatively high, it produces no disagreeable effects. This system of ventilation is superior to that which merely introduces fresh air from the outside, because it does not necessitate the heating of large amounts of cold air. A great saving in the fuel used for heating the building thus results.

86. How to get fresh air. Because the atmosphere in the country is really clean, it is well for everyone to *live as much as possible in the open air*. Since, however, a great deal of the world's work must be done indoors, it is important that we take every precaution to ventilate our houses properly. Some people have thought that night air is injurious, but a careful study shows that night air is the same as that which we breathe during the day. In fact, the proper ventilation of a sleeping room is one of the first requirements for good health. Since the exhaled air is usually warmer and lighter than the inhaled air, it rises to the top of the room. Therefore it is better to open a window *at the top* to let the hot upper air out and also *at the bottom* to admit the fresh air (Fig. 69). Of course, this does not mean that one should sleep in a strong draft. In many places it is feasible to sleep out of doors on a sleeping porch and so to secure perfect ventilation

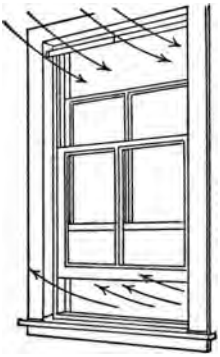

Fig. 69. Ventilation of a room by opening the window at top and bottom.

SUGGESTION

For further rules about healthful living, read *Fisher and Fisk's* How to Live. — Funk & Wagnalls Co.

SUMMARY OF CHAPTER VIII

ELEMENTARY NITROGEN forms about *four-fifths of the air.* Nitrogen compounds are *essential* to life.

PREPARED from the air by burning out the oxygen with phosphorus or with red-hot copper; this is sufficiently pure for most purposes.

PURE NITROGEN is prepared by heating ammonium nitrite (sodium nitrite and ammonium chloride), which gives water and nitrogen.

PROPERTIES: nitrogen is an inert substance. It is a colorless, odorless, tasteless gas; does not burn; does not support combustion or respiration; is not poisonous. It does not easily unite directly with other elements. At high temperatures it combines with a few metals such as magnesium, and also with oxygen and hydrogen.

AIR IS A MIXTURE, NOT A COMPOUND. It is essentially composed of nitrogen, oxygen, and argon with varying amounts of water vapor, carbon dioxide, and dust.

AIR CAN BE LIQUEFIED and separated into its components by allowing the more volatile parts to boil off first.

ARGON occurs in air to the extent of nearly one per cent by volume. There are traces of four other rare gases, which cannot be made to combine with any other elements. Argon is used for filling electric-light bulbs.

HELIUM is one of the rare gases; it can be made commercially by liquefying certain natural gases. It is noninflammable and seven times lighter than air. Used in balloons to some extent.

CARBON DIOXIDE is introduced into the air by combustion and respiration. It is removed by green plants, which get all their carbon from the carbon dioxide in the air and produce oxygen. This balance of plant and animal life keeps the amounts of oxygen and carbon dioxide in the air constant.

The *chief factors* in the air which affect *human comfort* are (1) moisture, (2) temperature, (3) dust, (4) small amounts of impurities given off by the human body. To get as much fresh air as possible, — *work, play,* and sleep out of doors.

QUESTIONS

1. How would you distinguish between nitrogen and carbon dioxide?

2. Of what use is the carbon dioxide in the air?

3. Why will an animal die in nitrogen gas?

4. Why are traces of nitrogen compounds found in the air after a thunderstorm?

5. Every ton of coal burned produces about 3 tons of carbon dioxide. Why does the composition of the air vary so little?

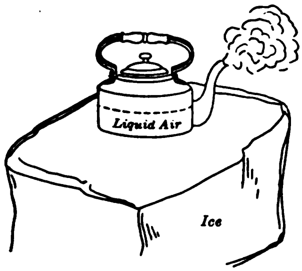

Fig. 70. Liquid air in the teakettle boils on a cake of ice.

6. If a teakettle containing liquid air is placed on a cake of ice, the liquid boils vigorously (Fig. 70). Explain.

7. Why do we not put a stopper in a bottle containing liquid air?

8. How would you prepare a sample of air which is free from water vapor and carbon dioxide?

9. If air has a definite composition, why is it not considered a compound?

10. State three ways in which oxygen can be removed from air.

11. Why are there so few nitrogen compounds among the minerals?

12. What are the principal objections to dust in the air we breathe?

13. How may one increase the humidity of the air in a room?

14. Why do not green plants produce as much oxygen at night as during the day?

15. What relief does an electric fan in a room offer on a hot day? Explain.

16. Why does the carbon dioxide not form a layer at the bottom of a room?

TOPIC FOR FURTHER STUDY

Ventilation. Investigate the ventilation of the classroom. The air currents may be observed by means of lighted bits of paper. Notice the effect of opening and closing the windows. What are the modern methods of ventilating schoolrooms, theaters, and public halls? Why is it not necessary to have a ventilating system in a dwelling-house? What methods can be used for regulating the temperature and the humidity?

CHAPTER IX

THE THEORY OF ATOMS AND MOLECULES

Three laws — conservation of matter, constant and multiple proportions — facts and theories — Dalton's theory of atoms — explanation of facts — atoms and molecules — physical and chemical changes — value of atomic theory.

87. Review of the three fundamental laws. In all our study of chemical substances and their changes we find that matter is indestructible; that is, *the sum of the weights of the substances which take part in a chemical change is equal to the sum of the weights of the products formed* (Law of Conservation of Matter).

We have also seen that one of the most important characteristics of a chemical compound is expressed by the Law of Definite Proportions: *the weights of the elements which combine to form a given compound are always in the same definite proportion.*

We further saw that *when two elements combine to form two or more compounds, the ratio of the weights of the one element combined with a fixed weight of the other in the two compounds can be expressed by small whole numbers.* This is the Law of Multiple Proportions. These laws are the general expressions of a vast number of well-established facts.

88. Facts and theories. Whenever we are confronted with a series of facts, we are prone to ask ourselves the question, Why are these facts so? To explain and account for **facts** chemists have adopted certain **theories.** It is worth while to see just what the difference is between laws and theories. A **law** may be defined as a generalization based on experimental facts; *it is a shorthand* method of summarizing the results of a large number of investigations. *A theory is a sort of scientific guess, or hypothesis, which we make in order to explain the facts.* If the hypothesis fits all the facts, it is considered a satisfactory theory so long as no new facts are discovered which disagree with it; but if fresh facts are found out which will not harmonize with the theory, it must be given up and a new one proposed.

FIG. 71. JOHN DALTON (1766–1844). An English schoolmaster and chemist who introduced the atomic theory.

A theory always starts with certain assumptions which we cannot test experimentally. Beginning with these assumptions, we reason that so and so must be true. The more closely the conclusions fit the known facts the more likelihood there is that the theory is correct. We cannot, however, say that the theory is proved, but merely that it is probably true.

89. What is the atomic theory? The early Greek philosophers (about 300 B.C.) believed that all matter was composed of very minute particles which could not be further subdivided. These ultimate bits of matter they called **atoms**. The ancient thinkers, however, had such a meager knowledge of natural science that they could not make use of this theory to explain natural phenomena. John Dalton (Fig. 71) in 1808 put forward a theory which explained very simply the Law of Definite and Multiple Proportions. Dalton, like the Greeks, assumed that all matter was composed of very minute particles, which he also called **atoms**; but aside from this fundamental assumption, his views were quite different from those of the early philosophers. His contribution, generally known as the **atomic**

theory, has been adopted to explain the facts about chemical compounds, and it may therefore justly be said to be the most comprehensive and useful theory in modern chemistry.

Dalton made the following assumptions:

(1) Matter is made up of small particles called atoms.

(2) All the atoms of a given element are exactly alike in size and weight, but differ in these respects from the atoms of every other element.

(3) Atoms can unite with other atoms and hold them by a force called chemical affinity; it is this union of atoms which produces chemical compounds.

(4) Atoms cannot be divided, and therefore only whole atoms unite with each other.

90. How this theory helps us to understand the facts. *First,* as to the fact that compounds always have a definite composition. According to this theory we assume that a compound is due to a union of atoms of different elements. For example, in carbon monoxide one atom of carbon unites with one atom of oxygen, forming a group of two atoms. Since all the oxygen atoms have exactly the same weight and the carbon atoms also have each a fixed weight, any sample of carbon monoxide will have a definite composition. This is the Law of Definite Proportions.

Second, as to the Law of Multiple Proportions. It is conceivable that a carbon atom might unite with two atoms of oxygen instead of only one. An entirely different compound would result; in each group there would be one carbon atom and *two* oxygen atoms. That is, there would be twice as much oxygen combined with carbon as in the first case. Carbon dioxide is, in fact, just such a substance: it contains twice as much oxygen as carbon monoxide. In carbon dioxide we imagine that every atom of carbon is united with two atoms of oxygen.

Finally, as to the Law of Conservation of Matter. We assume that in a chemical change the atoms are redistributed, but that none are produced or annihilated. The sum of the atoms of the substances which take part in a chemical reaction must equal the sum of the atoms in the products, since none are lost in the change. This simply means that matter is indestructible.

91. Atomic weights of the elements. Since the atoms are so very small we do not attempt to determine the actual weight of a single atom. But by comparing the relative weights of elements which combine, we have been able to determine with great precision the *relative weights* of their atoms.

The numbers which are now accepted by chemists as representing the atomic weights of the elements are given in the table in the back of the book. It will save time if we become familiar with the approximate atomic weights of some of the commoner elements. In this table we see that the atomic weight of carbon is 12 and of oxygen is 16. Therefore in carbon monoxide we should expect 12 parts by weight of carbon to unite with 16 parts by weight of oxygen; in other words, the ratio of carbon to oxygen would be as 1 : 1.33, which corresponds to the results of the chemical analysis of carbon monoxide. The fact is, as we shall see later (Chapter XIII), that the numbers in the table are derived from the relative combining weights of the elements in compounds. These weights are determined by very precise analysis of the compounds. Therefore the table of atomic weights represents certain chemical facts in regard to the elements which are quite independent of any theory.

92. Atoms and molecules. *The smallest indivisible part of an element is an atom.* We have already seen in Chapter V that a gas is composed of a vast number of minute particles called **molecules**. In most common gases, such as oxygen, nitrogen, and hydrogen, each molecule is made up of two atoms held together in chemical combination. In the case of a compound such as carbon monoxide (§ 68) the carbon and oxygen atoms are joined together in groups; these groups of atoms are molecules. A great number of such molecules make up the gas which we recognize as carbon monoxide. Thus, in certain elementary gases a molecule is composed of two atoms of the *same* element; in a compound a molecule is composed of two or more atoms of *different* elements. There are a few cases, such as mercury vapor, where the molecules of the gas are the atoms themselves; these gases are said to have monatomic molecules.

93. Physical and chemical changes. When a gas, such as air, is liquefied, we think of the molecules as coming closer together in the space they occupy; and again, when the liquid is frozen, we imagine the molecules as coming still closer together so that they attract each other with considerable force. But in all these states of matter we conceive of the molecules as vibrating, and the temperature of a body as an outward indication of the rapidity of this vibratory motion. These *changes which affect the molecule as a whole we call physical changes.*

If, however, we disturb the composition of the molecule by breaking through the force which unites the atoms, we produce **a chemical change.** For example, when we separate the constituent atoms in the water molecules and obtain hydrogen and oxygen, which are both entirely different in their properties from the original water, this is a chemical change.

We may define *an atom as the smallest particle of an element which can take part in a chemical change.* We may also define ***a molecule*** *as the smallest particle of matter which can exist in a gaseous state.*

94. Value of the atomic theory. If the theory of atoms is merely an hypothesis about the atoms, which are so small that we cannot see them, why study the theory at all? It is an interesting fact that although it is more than a hundred years old, it has *never been* replaced by a better one. Chemists generally agree that it does explain satisfactorily the facts regarding chemical combination, and that it has done more than any other theory for the advancement of the physical sciences. In recent years an abundance of new experimental evidence has been found, which we cannot here describe in detail since it involves considerable mathematical physics. The atomic theory has been so strengthened by all this work that scientists have come to believe in the existence of atoms and molecules with as much certainty as is possible about things which we cannot see by direct observation.

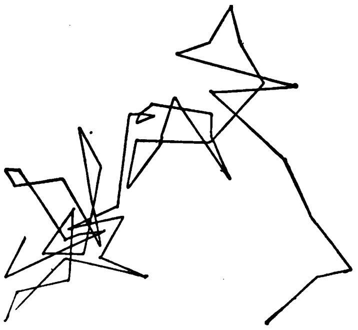

Fig. 72. Path of a Brownian particle as observed under a microscope.

95. Brownian Movement. If very fine particles are suspended in a liquid and the mixture examined under a very powerful microscope, it will be seen that all the particles are in a state of rapid and irregular motion. This is called the **Brownian Movement,** and is apparent only with particles which are so small that they cannot be seen except with a microscope. While scientists have known of the movement of these particles for a long time, it has only recently been carefully studied. The thorough investigation of this problem has led to one of the most convincing arguments as to the reality of molecules.

The motion never ceases and is independent of the nature of the particles; liquids taken from the interior cavities of rocks, which must have been sealed up for eons, show the same Brownian Movement. This motion of the minute particles is almost certainly due to the fact that they are being bombarded by the molecules of the liquid, which are themselves in constant motion. A liquid, like a gas, is also made up of molecules, but they are in closer contact with each other. The Brownian particles serve, then, to visualize this never-ending dance of the molecules. While we cannot yet observe the molecules themselves, we can see them move and toss around a somewhat larger particle of matter (Fig. 72).

It has been possible in several ways to estimate the size of a molecule. The diameter of a molecule is somewhere in the order of $\frac{3}{100,000,000}$ of a centimeter. The smallest particle which can be seen with a microscope is about $\frac{2}{100,000}$ of a centimeter in diameter.

SUMMARY OF CHAPTER IX

THE ATOMIC STRUCTURE of matter was first suggested by early Greek philosophers. John Dalton in 1808 used it as a basis for a theory which explained the Laws of Definite and Multiple Proportions.

DALTON'S THEORY assumes the following:

(1) All matter is composed of atoms.

(2) All atoms of a given element are alike.

(3) Atoms can unite with and hold other atoms by reason of a force called chemical affinity.

(4) Atoms are indivisible, and therefore only whole atoms can unite with one another.

AN ATOM is the smallest particle of an element which can take part in a chemical change.

A MOLECULE is the smallest particle of matter which can exist in a gaseous state.

A LAW is a generalization of experimental *facts;* a *theory* involves certain assumptions from which certain conclusions may be drawn to explain a series of experimental facts. An *hypothesis* is a scientific guess which, if satisfactory, may become a theory.

THE ATOMIC THEORY is still a theory, but science has recently developed considerable evidence which makes the reality of atoms and molecules extremely probable.

QUESTIONS

1. Show how the Law of Conservation of Matter applies to the decomposition of red oxide of mercury.

2. Show how the Law of Definite Proportions applies to the composition of water.

3. Sulfur dioxide is 50% sulfur and 50% oxygen. Sulfur trioxide is 40% sulfur and 60% oxygen. Show how these facts illustrate the Law of Multiple Proportions.

4. State in your own words the four assumptions which Dalton made in his atomic hypothesis.

5. What is the difference between an hypothesis and a theory?

6. What is the difference between a natural law and a state law?

7. What theory accounts for the effects of temperature and pressure upon the volumes of gases?

8. What is meant by the terms: (*a*) atom of an element, (*b*) molecule of an element, (*c*) molecule of a compound?

9. Classify the following as either physical or chemical changes: (*a*) the burning of wood, (*b*) the evaporation of gasolene, (*c*) the dissolving of sugar in water, (*d*) the souring of milk, (*e*) the melting of butter, (*f*) the decay of food, (*g*) the explosion of dynamite.

TOPIC FOR FURTHER STUDY

Science in ancient Greece and Rome. Why did not the early Greek philosophers apply their idea of the atomic theory to explaining chemical facts? Were they interested in chemistry and physics? (*Moore's* History of Chemistry, and *Sedgwick and Tyler's* Short History of Science.)

CHAPTER X

SYMBOLS, FORMULAS, AND EQUATIONS

Symbols, significance — formulas, significance — percentage composition calculation — chemical equations — how to write equations — five steps — what an equation does not show — review equations of reactions studied.

Five types of reactions — reversible reactions.

96. Chemical symbols. Chemists have found it convenient to represent the various elements by the symbols which are given in the table on the back cover. These symbols were introduced by the Swedish chemist, Berzelius (Fig. 73), and are merely the first letter or letters of the names of the elements; as, for instance, C for carbon, H for hydrogen, O for oxygen, S for sulfur, Br for bromine, and Si for silicon. In a few cases the first letter and one other that is prominent in the name are used, such as Cl for chlorine and Mg for magnesium. In other cases the symbol is taken from the Latin name; thus, Cu stands for copper (*cuprum*), Fe for iron (*ferrum*), Ag for silver (*argentum*). It will be well for the

FIG. 73. JOHANN JACOB BERZELIUS (1779–1848).

Introduced the modern symbols used in chemistry.

student to learn the symbols of the common elements as we study them.

97. What does a symbol mean? These symbols are not used as *mere* shorthand signs, but each one stands for *an atom* of the element. Thus, the symbol O stands for one atom of oxygen, and the symbols H, N, Na, Fe represent one atom of hydrogen, nitrogen, sodium, and iron, respectively, and not these substances in general. More exactly, then, they are *atomic symbols,* and not merely abbreviations of the names of the elements.

We have also seen that the *atoms have a perfectly definite weight,* and so the symbol means not only the element but a definite quantity of the element. O always means 16 parts by weight of oxygen, and C always means 12 parts by weight of carbon.

When we know how many atoms of an element go to make up a molecule of that element, we can express this knowledge very briefly by symbols with small subscripts placed after them. Presently we shall show that the molecule of hydrogen, oxygen, nitrogen, chlorine, and some others consists of two atoms; this fact is represented by the symbols H_2, O_2, N_2, Cl_2, respectively. The symbol H_2 thus means *one molecule of hydrogen.*

98. Chemical formulas. We may represent the composition of compounds with these symbols. This is done simply by placing side by side the symbols for the various elements in the compound. For example, sodium chloride (common salt) is made of one atom of sodium (Na) and one atom of chlorine (Cl) and is represented by the united symbols of the two elements, NaCl. Such an arrangement of symbols representing a compound is called the formula of that compound.

When the molecules of a compound contain more than one atom of any particular element, this fact, as we have said, is expressed by placing small numbers immediately after the symbol of that element. Thus, H_2O is the formula for one molecule of water, a compound containing two atoms of hydrogen and one atom of oxygen. Very often it is necessary to indicate a group of atoms in a molecule which behave in many reactions like a single atom. Parentheses are used for this purpose. Thus, a molecule of calcium hydroxide (limewater) may be represented by $Ca(OH)_2$, which indicates a molecule containing one atom of calcium, two atoms of oxygen, and two atoms of hydrogen.

When we wish to indicate more than one molecule of any substance, we place large numerals before the symbol or formula. Thus, $2\ O_2$ means two molecules of oxygen, and $5\ H_2O$ means five molecules of water.

99. Just what does a formula mean? It is very important that we understand the full meaning of a formula. For example, the formula for sulfuric acid is H_2SO_4, which means:

(1) one molecule of sulfuric acid;

(2) composed of two atoms of hydrogen, one atom of sulfur, and four atoms of oxygen;

(3) 2 parts by weight of hydrogen, 32 parts by weight of sulfur, and 4×16 or 64 parts by weight of oxygen;

(4) $2 + 32 + 64$ or 98 parts by weight of sulfuric acid.

100. Percentage composition from the formula. If we know the formula of a compound and have a table of atomic weights, we can easily calculate the percentage of each element in the compound. Given the formula of potassium chlorate as $KClO_3$, and the atomic weight of potassium 39, of chlorine 35.5, and of oxygen 16. Then the formula represents

	39.0	parts by weight of potassium,
	35.5	parts by weight of chlorine, and
3 × 16 or	48.0	parts by weight of oxygen,
or	122.5	parts by weight of potassium chlorate.

Therefore potassium chlorate contains

$$\frac{39}{122.5} = 0.318 \text{ or } 31.8 \text{ per cent of potassium,}$$

$$\frac{35.5}{122.5} = 0.290 \text{ or } 29.0 \text{ per cent of chlorine, and}$$

$$\frac{48}{122.5} = 0.392 \text{ or } 39.2 \text{ per cent of oxygen.}$$

QUESTIONS AND PROBLEMS

1. Give the symbol of each of the following elements: sodium, sulfur, manganese, magnesium, mercury, potassium, phosphorus, lead, platinum, and iron.

2. Name the elements which correspond to the following symbols: Ag, Sn, W, Ni, Au, Cu, A, Ra, As, and Al.

3. State the facts expressed by the formulas: $CuSO_4$, $3\,NaCl$, $2\,H_2O$, P_4, and $Ba(OH)_2$.

4. Compute the percentage composition of the following compounds from the formulas as given: (*a*) common salt (NaCl); (*b*) saltpeter (KNO_3); (*c*) mercuric oxide (HgO); (*d*) sulfuric acid (H_2SO_4); and (*e*) cane sugar ($C_{12}H_{22}O_{11}$).

NOTE. Use the approximate atomic weights as given on back cover.

101. Chemical equations. The principal use which the chemist makes of symbols and formulas is in writing in a condensed and precise form a large amount of information about chemical changes, or reactions. Inasmuch as matter is indestructible (Law of Conservation of Matter), *we represent these changes, or reactions, as* ***equations.*** There is the same amount of each element after the change as before.

The symbols and formulas of all the *materials undergoing change* are placed on the *left;* those of the new *products* resulting from the change, on the *right;* the *arrow* means *forms* or *gives.* For example, the union of iron and sulfur to form iron sulfide is expressed thus:

$$Fe + S \longrightarrow FeS$$

The burning of magnesium in oxygen might at first be expressed thus:

$$Mg + O_2 \longrightarrow MgO$$

but this equation is **wrong** because we have *two* atoms of oxygen on the left and *only one* on the right side, and this would indicate that some of the oxygen had been lost. The very word "equation" means that there must be just as many atoms of each element after the change (on the right) as before (on the left). We can " balance " the equation, as it is called, thus:

$$2\,Mg + O_2 \longrightarrow 2\,MgO$$

In decomposing potassium chlorate by heat we might write the equation at first thus:

$$KClO_3 \longrightarrow KCl + O_2$$

and then balance it thus:

$$2\,KClO_3 \longrightarrow 2\,KCl + 3\,O_2$$

From a study of the above it will be seen that these equations are not algebraic; they represent chemical changes which actually take place. Before we can write an equation we must know:

(1) *that the change takes place;*

(2) *what substances are involved;*

(3) *what the products are; and*

(4) *the formulas of all the substances involved and of all products.*

102. How to write equations. In making a chemical equation there are *five* steps:

(1) Write *on the left* the formula of each substance taking part in the reaction.

(2) Write *on the right* the formula of each substance known to be produced.

(3) Correct the right-hand side by increasing the number of molecules so as to use all the elements on the left.

(4) Correct the left-hand side by increasing the number of molecules needed by the substances produced.

(5) Check up to make sure that each atom of all the elements is accounted for.

FOR EXAMPLE, hydrogen burns in oxygen and produces water.

(1) H_2+O_2

(2) $H_2+O_2 \longrightarrow H_2O$

(3) $H_2+O_2 \longrightarrow 2\,H_2O$

(4) $2\,H_2+O_2 \longrightarrow 2\,H_2O$

(5) We have 4 atoms of hydrogen in the 2 molecules of hydrogen on the *left*, and we have 4 atoms of hydrogen in the 2 molecules of water on the *right*. We have 2 atoms of oxygen in 1 molecule of oxygen on the *left*, and we have 2 atoms of oxygen in the 2 molecules of water on the *right*.

103. Cautions. Use the **molecular formulas** for the gaseous elements. Thus, the molecular formulas of oxygen, hydrogen, nitrogen, and chlorine are O_2, H_2, N_2, Cl_2.

Remember that the number placed before a formula multiplies the *whole* formula. Thus, $2\,H_2O$ is the same as $2(H_2O)$, which means two molecules of water consisting of 4 atoms of hydrogen and 2 atoms of oxygen.

We balance equations *not* by altering the formulas of the substances, but by taking the proper number of molecules so that the number of atoms of each element is the same on both sides.

104. What an equation does not show. Chemical changes will usually occur only under certain *conditions*, which are not indicated in the equation.

For example, the equation

$$2\,HgO \longrightarrow 2\,Hg + O_2$$

does not show that it is necessary to keep heating the red oxide of mercury in order to decompose it. The equation

$$Zn + H_2SO_4 \longrightarrow ZnSO_4 + H_2$$

does not indicate that the sulfuric acid must be diluted with water.

In general, the materials which are present but which undergo no change, such as water used as a solvent and the various catalysts, are not represented in the equation. Finally, we do not as a rule try to show the amount of heat which is evolved in the chemical reaction. For example,

$$C + O_2 \longrightarrow CO_2$$

shows that carbon unites with oxygen to form carbon dioxide; but it does not tell us *how much heat is produced*, a piece of information which is most important for the industrial chemist.

105. Equations for reactions studied. We shall now write chemical equations for the reactions which we have studied up to this point, and which we have hitherto summarized by words. *The student will do well to master thoroughly all these equations.*

When water is electrolyzed it is decomposed into free hydrogen and oxygen. The equation for this is:

$$2\ H_2O \longrightarrow 2\ H_2 + O_2$$

We have to take two molecules of water in order to provide two oxygen atoms, since the formula for free oxygen is O_2.

When mercury oxide is heated oxygen and mercury result. The equation is:

$$2\ HgO \longrightarrow 2\ Hg + O_2$$

Again we take two molecules of mercury oxide, so that we may have enough oxygen atoms to form a molecule. The mercury formed is a liquid; and we have reason to believe that the atoms in metals are often not united in molecules. Hence we represent them as in this case: 2 Hg *not* Hg_2, two single atoms of mercury, *not* a molecule of mercury composed of two atoms.

FIVE TYPES OF REACTIONS

106. Simple decomposition. This type of chemical change involves only one substance, which breaks down by chemical change into two or more simpler substances. Such a reaction is called a **simple decomposition**. The decomposition of water into hydrogen and oxygen is an example of this type of chemical change.

107. Direct combination or synthesis. Another type of chemical reaction, which is the *reverse* of simple decomposition, is **synthesis**. In this type we start with two or more substances and build up a compound. The following equations are the syntheses involving oxygen which we have thus far considered:

$$2\ Hg + O_2 \longrightarrow 2\ HgO$$
$$2\ H_2 + O_2 \longrightarrow 2\ H_2O$$
$$C + O_2 \longrightarrow CO_2$$
$$4\ P + 5\ O_2 \longrightarrow 2\ P_2O_5$$
$$2\ C + O_2 \longrightarrow 2\ CO$$
$$2\ CO + O_2 \longrightarrow 2\ CO_2$$

These equations represent the changes which took place when mercury, hydrogen, carbon, and phosphorus were heated in contact with pure oxygen or air. The last two equations show the burning of carbon in an insufficient supply of oxygen, producing carbon monoxide; and then the burning of carbon monoxide to carbon dioxide.

108. Simple replacement. The methods of preparing hydrogen (except the electrolysis of water) are examples of a type of chemical change called **replacement**. In this type of reaction one element takes the place of some other element or elements in a compound.

Thus, when zinc or magnesium acts on hydrochloric acid or sulfuric acid, the metal replaces the hydrogen:

$$Zn + 2\ HCl \longrightarrow ZnCl_2 + H_2$$
$$Zn + H_2SO_4 \longrightarrow ZnSO_4 + H_2$$
$$Mg + 2\ HCl \longrightarrow MgCl_2 + H_2$$

When steam is passed over hot iron, the iron replaces the hydrogen of the water, forming the magnetic oxide of iron (Fe_3O_4):

$$4\ H_2O + 3\ Fe \longrightarrow Fe_3O_4 + 4\ H_2$$

When metallic sodium or calcium is placed in water, the metal replaces the hydrogen of the water, forming sodium hydroxide ($NaOH$) or calcium hydroxide ($Ca(OH)_2$):

$$2\,Na + 2\,H_2O \longrightarrow 2\,NaOH + H_2$$

$$Ca + 2\,H_2O \longrightarrow Ca(OH)_2 + H_2$$

NOTE that in order to be able to represent the hydrogen in the molecular state (H_2) we must prefix the coefficient 2 in several places.

109. Double decomposition. Probably the commonest type of chemical reaction involves the interaction of two compounds to produce two other compound products. This is called **double decomposition** because each compound apparently breaks up into two parts, each of which unites with a different part of the other compound.

FOR EXAMPLE, take the reaction of hydrochloric acid (HCl) on marble ($CaCO_3$) to form calcium chloride ($CaCl_2$) and carbonic acid (H_2CO_3):

$$2\,HCl + CaCO_3 \longrightarrow CaCl_2 + H_2CO_3$$

The carbonic acid decomposes into water (H_2O) and carbon dioxide (CO_2):

$$H_2CO_3 \longrightarrow H_2O + CO_2$$

110. Oxidation and reduction. The significance of oxidation and reduction has already been considered. We need now simply to write equations for some of the cases which we have met:

$$CuO + H_2 \longrightarrow Cu + H_2O \quad (\S\ 37)$$

$$CO_2 + C \longrightarrow 2\,CO \quad (\S\ 69)$$

111. Reversible reactions. When we dissolve carbon dioxide gas in water, there is a combination between the water and the carbon dioxide to form the compound carbonic acid:

$$H_2O + CO_2 \longrightarrow H_2CO_3$$

If we heat such a solution of carbonic acid the carbon dioxide gas is driven off and we finally end with only water:

$$H_2CO_3 \longrightarrow H_2O + CO_2$$

This reaction is just the reverse of the first; whether the reaction goes one way or the other depends on the conditions, in this case primarily on the temperature. We call such a reaction a **reversible reaction** and indicate it by writing a double arrow; thus:

$$H_2O + CO_2 \rightleftharpoons H_2CO_3$$

This equation tells us that the reaction will proceed one way or the other according to the conditions.

SUMMARY OF CHAPTER X

THE CHEMICAL SYMBOL of an element represents one atom of the element; it also signifies the atomic weight of the element, usually in grams.

THE FORMULA of a compound shows what elements constitute the compound, and also the percentage composition.

AN EQUATION represents an actual chemical reaction. It is a picture of the molecular condition of a certain number of atoms before and after a chemical change.

A chemical equation must always be *balanced;* it must have the same number of atoms of each element on one side as on the other.

BEFORE WE CAN WRITE AN EQUATION WE MUST KNOW:

(1) that the change takes place;
(2) what substances are involved;
(3) what the products are;
(4) the formulas for all the substances involved and all the products.

A chemical equation *does not indicate* the conditions of the reaction. Catalysts and solvents, which are not affected, are not expressed. Usually the heat effects are not indicated.

CHEMICAL CHANGES CAN BE CLASSIFIED AS

(*a*) simple decomposition, (*b*) direct combination,
(*c*) simple replacement, (*d*) double decomposition, or
(*e*) oxidation and reduction.

A REVERSIBLE REACTION is one in which the reaction may proceed in either direction according to conditions.

Questions and Problems

1. What is the distinction between a symbol and a formula? Illustrate each.

2. State the meaning of each figure and letter in the following formulas: $2\ H_2SO_4$; $10\ H_2O$; $(NH_4)_2SO_4$; $Fe_2(SO_4)_3$.

3. Calculate the percentage composition of the following compounds: black copper oxide (CuO); carbon dioxide (CO_2); marble ($CaCO_3$); iron oxide (Fe_3O_4); zinc sulfate ($ZnSO_4$).

HINT. Use table of approximate atomic weights on back cover.

4. Why is a chemical equation called an *equation?*

5. What is the difference between O_2 and $2\ O$?

6. What is the difference between simple decomposition and double decomposition?

7. Write a reversible equation involving hydrogen and oxygen. State the conditions under which it goes in each direction.

8. When zinc and sulfur are heated together, zinc sulfide (ZnS) is formed. Write the equation.

9. When aluminum reacts with hydrochloric acid (HCl), hydrogen and aluminum chloride ($AlCl_3$) are formed. Write the equation.

10. When tin is heated in the air, tin oxide (SnO_2) is formed. Write the equation.

11. When carbon dioxide is bubbled through limewater ($Ca(OH)_2$), calcium carbonate ($CaCO_3$) and water are produced. Write the equation.

12. Write the reversible equation for the classic experiment of Lavoisier with mercury and air.

CHAPTER XI

CHEMICAL CALCULATIONS

Importance — quantitative meaning of equations — problems involving weight only — significant figures — problems involving weight and volume — general rules.

112. Importance of calculations. To the industrial chemist the chemical equation is very important because it enables him to *calculate* just how much material he ought to use in a given reaction and how large a product he may hope to get. In actual practice, however, he very seldom gets the full amount of the product as calculated from the equation, and therefore he computes the efficiency of his process. These computations are all based on the chemical equations of the reactions, and require only the simplest arithmetical work.

113. Quantitative meaning of equations. An equation when properly balanced tells us what substances react and what the products are; it also gives us the number of molecules of each substance involved; finally, *by using the atomic weights, we learn the relative weights of the different substances in the equation.*

FOR EXAMPLE, in the equation for preparing oxygen by heating potassium chlorate we may compute the relative weights of potassium chlorate, potassium chloride, and oxygen thus:

$$\begin{array}{ccccc} 2\,KClO_3 & \longrightarrow & 2\,KCl & + & 3\,O_2 \\ (2 \times 122.5) & & (2 \times 74.5) & & (3 \times 32) \\ 245 & & 149 & & 96 \end{array}$$

The weight of each molecule (**molecular weight**) may be found by adding the atomic weights of the elements involved:

mol. wt. of $KClO_3 = 39 + 35.5 + (3 \times 16) = 122.5$
mol. wt. of $KCl = 39 + 35.5 = 74.5$
mol. wt. of $O_2 = 2 \times 16 = 32$

Since there are two molecules of potassium chlorate and of potassium chloride in the equation, we multiply their molecular weights by two; and as there are three molecules of oxygen, we multiply its molecular weight by three.

We can now read this equation as follows: *245 parts by weight of potassium chlorate give 149 parts by weight of potassium chloride and 96 parts by weight of oxygen.*

114. Problems involving weight only. What weight of iron sulfide (FeS) can be made with 10 grams of iron? Assume the necessary sulfur is available.

To avoid mistakes it is well to arrange the work very clearly and to do it methodically.

We *first* write the equation:

$$Fe + S \longrightarrow FeS$$

Then we write under each symbol and formula the weight it represents (using the atomic weights given on the back cover):

$$\underset{56}{Fe} + \underset{32}{S} \longrightarrow \underset{88}{FeS}$$

This means that 56 parts by weight of iron combined with 32 parts by weight of sulfur will give 88 parts by weight of iron sulfide. *We have here the quantitative meaning of the equation.*

Next we again read the problem and place above the symbol for iron the weight given, which is 10 g., and above the formula for iron sulfide an x, which is the weight we wish to find; thus:

$$\underset{56}{\overset{10}{Fe}} + \underset{32}{S} \longrightarrow \underset{88}{\overset{x}{FeS}}$$

Finally we state the proportion thus:

$$56 : 88 :: 10 : x$$

Hence $x = \dfrac{88 \times 10}{56}$ or **15.7 grams.**

Now we shall check up the reasonableness of our answer by roughly estimating what it ought to be. In this case we know that 56 parts of iron will give 88 parts of iron sulfide. Therefore we ought to get about one and a half times as much iron sulfide as the iron with which we started. Hence our answer, 15.7, is reasonable. In this way we may quickly detect such a mistake as the misplacing of a decimal point or the inverting of the proportion.

115. Significant figures. The atomic weights which are to be used in calculating such problems are the **approximate values** given in the table on the back cover. These are not the most accurate values which have been determined, but they are close enough for practical purposes. It is only in very accurate chemical work that we use the most exact values that have been obtained. It will be seen that these numbers have not more than *three figures* in them; the fourth, fifth, or sixth figure counting from the left has been rounded off. For example, the accurate atomic weight of barium is 137.37. We call this 137. In the same way, in carrying out arithmetical processes *we should express the answer in the nearest three figures.* Since we have used atomic weights that have not more than three figures in them, the fourth, fifth, and sixth figures in a possible answer will have no significance. We therefore say that the problems in this book should be carried to but *three significant figures.* Zeros which occur before a set of numbers, as for example in 0.00672, are not considered as significant figures; the three significant figures here are 6, 7, and 2.

116. Problems involving weight and volume. Suppose we wish to find out how many liters of carbon dioxide (measured under standard conditions) can be obtained from 2 kilograms of marble by the action of hydrochloric acid.

First, we write the complete equation for the reaction:

$$CaCO_3 + 2\ HCl \longrightarrow CaCl_2 + H_2O + CO_2$$

Second, we write under each formula the figure representing the weight for which each complete formula stands:

$$\underset{100}{CaCO_3} + 2\,\underset{73}{HCl} \longrightarrow \underset{111}{CaCl_2} + \underset{18}{H_2O} + \underset{44}{CO_2}$$

Third, we write above the equation what we know and what we desire to know about each of the substances involved:

$$\underset{100}{\overset{2000}{CaCO_3}} + 2\,\underset{73}{HCl} \longrightarrow \underset{111}{CaCl_2} + \underset{18}{H_2O} + \underset{44}{\overset{x}{CO_2}}$$

Fourth, we read the equation and the figures as they now stand and make a proportion which will show the required value:

$$100 : 44 :: 2000 : x$$

Fifth, we solve this proportion and check our answer:

$$x = \frac{44 \times 2000}{100} = \textbf{880 grams.}$$

Finally, we look up the density of carbon dioxide (see table in Appendix), and find it to be about 1.98 grams per liter.

Therefore the volume $= \frac{880}{1.98} =$ **444** liters.

NOTE. If the conditions were not standard (0° C. and 760 mm.), we should simply solve as above and reduce the volume under standard conditions to that under the required conditions, as explained in Chapter V.

Again, suppose the problem to be as follows: How much zinc is required to produce 10 liters of hydrogen (standard conditions) by the action of dilute sulfuric acid?

We must first find the weight of the hydrogen and then compute the weight of the zinc needed.

The weight of 10 liters of hydrogen is 10×0.09 or 0.90 grams.

The equation is as follows:

$$\underset{65}{\overset{x}{Zn}} + \underset{98}{H_2SO_4} \longrightarrow \underset{161}{ZnSO_4} + \underset{2}{\overset{0.90}{H_2}}$$

The proportion is $2 : 65 :: 0.90 : x$

$$\text{Therefore } x = \frac{65 \times 0.90}{2} = \textbf{29.3 grams.}$$

NOTE. If the volume of the hydrogen had not been measured under standard conditions, the first step would have been to reduce the volume to standard conditions, for the density of hydrogen (0.09 grams per liter) applies only to standard conditions.

117. General rules. Let us sum up in five general rules *the method used in solving chemical problems:*

(1) Write the complete equation for the reaction in question.

(2) Write under each formula the figure representing the weight for which each complete formula stands.

(3) Write above the equation what we know and desire to know about each of the substances involved in the reaction.

(4) Read the equation and the figures as they now stand and make a proportion which will show the required value.

(5) Solve this proportion and decide whether the answer is reasonable by making a rough calculation as to what the answer should be.

SUMMARY OF CHAPTER XI

A CHEMICAL EQUATION represents the *relative weights* of each of the substances involved. By *writing* out equations and then by using atomic and molecular weights, it is possible to calculate how much of any substance may be required or produced in a chemical change.

THE ACTUAL WEIGHTS of the substances are in the *same ratio* as the *weights of the molecules* involved. Such calculations deal with *but two* of the substances at a time.

PROBLEMS INVOLVING WEIGHT AND VOLUME may be solved first by finding the weight of the gas involved and then by computing the volume from the density. Or, if the volume is given, compute the weight and solve by proportion.

PROBLEMS

1. How much potassium chlorate must be used to generate 2 grams of oxygen?

2. How much mercuric oxide must be used to generate 2 grams of oxygen?

3. What weight of zinc will be needed to generate 100 liters of hydrogen, using dilute sulfuric acid?

4. What weight of zinc will be needed to generate 100 liters of hydrogen, using dilute hydrochloric acid?

5. Calculate the weight of hydrogen generated when 100 cc. of dilute sulfuric acid containing 25 grams of pure sulfuric acid is added to 10 grams of zinc.

6. What volume of hydrogen (measured under standard conditions) could be obtained by the electrolytic decomposition of 5 grams of water?

7. What volume of hydrogen (measured under standard conditions) is needed to reduce 10 grams of copper oxide (CuO)?

8. How many grams of mercury would result from the complete decomposition of 5 grams of mercuric oxide?

9. What weight of zinc is required to make 10 liters of hydrogen (at 15° C. and 745 mm.) by replacement from sulfuric acid?

10. What volume of carbon dioxide (measured under standard conditions) would be given off from 1 kilogram of sodium bicarbonate in a fire extinguisher? The equation is

$$2\,NaHCO_3 + H_2SO_4 \longrightarrow 2\,CO_2 \uparrow + 2\,H_2O + Na_2SO_4$$

TOPIC FOR FURTHER STUDY

Practical chemical calculations. Suppose hydrogen is desired for balloons. How much would the raw materials cost for making 100,000 cu. ft. of the gas from (*a*) zinc and acid; (*b*) iron and acid? What would be the cheapest acid to employ? Which of these methods would seem to be the more economical? There are other important items of expense beside raw materials; a final answer to the cost of manufacturing hydrogen could be given only if these other expenses were known. What methods were used to prepare hydrogen for the balloons used in the World War? (Market prices of materials will be found in trade journals, such as *Chemical and Metallurgical Engineering*.)

CHAPTER XII

HYDROGEN CHLORIDE

Common salt and sulfuric acid — laboratory and commercial preparation of hydrogen chloride — properties — hydrochloric acid — acids in general — bases — neutralization — chlorides — test for a chloride — uses of hydrochloric acid — composition of hydrogen chloride by electrolysis and by synthesis.

118. Action of common salt and sulfuric acid. Thus far we have been principally concerned with water and its constituent elements, and with the air and its components. Another very familiar substance is common salt, or **sodium chloride** ($NaCl$). **Sulfuric acid** (H_2SO_4), a chemical with which we have already worked, is doubtless the most important substance which the chemist uses. Let us find out what happens when this acid is added to common salt.

We place a pinch of sodium chloride in a test tube and add a few drops of concentrated sulfuric acid. If necessary we warm it slightly in order to start the action. We soon see bubbles of gas forming on the salt and rising through the acid, and we smell a sharp, choking odor. The gas itself has no color, but when we blow over the top of the tube a white cloud is formed. A piece of moist blue litmus paper *turns from blue to red* when we bring it near the mouth of the tube. If we bring near the open end of the tube a piece of filter paper wet with ammonia water, a very dense white smoke appears. These are the characteristics of a gas known as **hydrogen chloride** (HCl).

119. Preparation of hydrogen chloride. In order to study further the properties of hydrogen chloride we may set up the apparatus shown in figure 74. The flask contains a handful of common salt. The sulfuric acid is introduced through a thistle tube which reaches nearly to the bottom of the flask. Since the gas (HCl) is extremely soluble in water, we cannot collect it over water. It is, however, heavier than air; so we may collect it in an open bottle by *downward displacement* of the air. Heat must be applied *very gently* when it is necessary. The presence of the gas in the bottle is recognized by the pungent odor and by the white fumes which appear when the breath is blown over the top of the bottle.

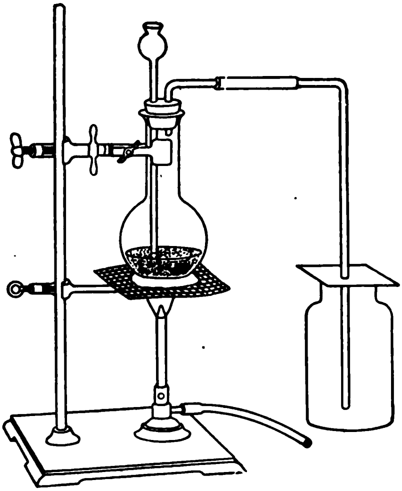

Fig. 74. **Hydrogen chloride generator.**

The method used in manufacturing hydrogen chloride on a commercial scale is not different in principle from that just described. When sulfuric acid (H_2SO_4) and sodium chloride (NaCl) react, the hydrogen of the acid combines with the chlorine of the salt to form the gas hydrogen chloride (HCl), which is given off. There is left behind in the flask or retort a white solid which is called sodium sulfate (Na_2SO_4). This reaction can be expressed thus:

$$\underset{\text{sulfuric acid}}{H_2SO_4} + \underset{\text{sodium chloride}}{2\,NaCl} \longrightarrow \underset{\text{sodium sulfate}}{Na_2SO_4} + \underset{\text{hydrogen chloride}}{2\,HCl} \uparrow$$

It will be noted that this is an example of **double decomposition** and that one of the products is a gas. This is indicated by the arrow pointing *up*. Sulfuric acid is used because it boils at a comparatively high temperature (338° C.), while hydrogen chloride is a gas at room temperatures.

120. An experiment with hydrogen chloride. The extreme solubility of this gas in water may be strikingly shown in the following experiment:

We fill a dry flask with the gas and insert in it a two-hole rubber stopper in one hole of which is a " dropper " containing water and in the other a straight glass tube drawn down to a small opening on the inside end. The apparatus is set up as shown in figure 75. Next we pinch the rubber bulb, expelling a few drops of water into the flask. This water dissolves so much of the gas that the water in the jar is forced by atmospheric pressure to behave like a fountain.

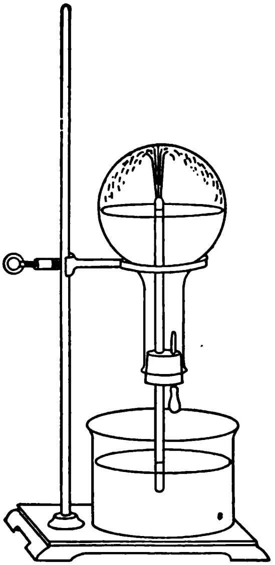

Fig. 75. Hydrogen chloride is extremely soluble in water.

It is this great solubility of hydrogen chloride in water which causes the characteristic fuming of the gas in moist air. The moisture of the air dissolves the gas and then forms small droplets of the solution, which remain suspended in the air like white fog.

121. Properties. Hydrogen chloride is a colorless gas, about one-fourth heavier than air. It has a very irritating, sharp odor and is extremely soluble in water: one cubic centimeter of water dissolves between 400 and 500 cubic centimeters of the gas. Hydrogen chloride will not burn and will not support combustion. The dry gas reacts only very slowly with most metals at room temperature. It will react with some at a high temperature. The hydrogen of the compound is liberated as hydrogen gas, and the chlorine combines with the metal (simple replacement).

It reacts with zinc and the product is zinc chloride ($ZnCl_2$), a white solid. The equation for the reaction is:

$$\underset{\text{zinc}}{Zn} + \underset{\text{hydrogen chloride}}{2\,HCl} \longrightarrow \underset{\text{zinc chloride}}{ZnCl_2} + \underset{\text{hydrogen}}{H_2\uparrow}$$

The above reaction is exactly analogous to that between steam and iron to give hydrogen and iron oxide. The equation for this reaction is:

$$\underset{\text{iron}}{3\,Fe} + \underset{\text{steam}}{4\,H_2O} \longrightarrow \underset{\text{iron oxide}}{Fe_3O_4} + \underset{\text{hydrogen}}{4\,H_2\uparrow}$$

122. Hydrochloric acid. The solution of hydrogen chloride in water is known as **hydrochloric acid.** Its properties are quite different from those of the dry gas, and the two substances should not be confused. Solutions of the gas in water containing as much as 40 per cent by weight of the gas can be prepared. A solution containing more than 30 per cent of the gas is called **concentrated hydrochloric acid.** This is the concentration of the commercial acid which is known as "muriatic acid." When it is diluted with 3 or 4 times its volume of water, we have **dilute** hydrochloric acid. A concentrated solution of the pure gas in distilled water is "chemically pure" (C. P.) hydrochloric acid. This is a colorless liquid with a density of about 1.2 grams per cubic centimeter.

Hydrochloric acid is a very active substance. We have already used it for preparing carbon dioxide (§ 63). It reacts vigorously with zinc, producing hydrogen. In fact, with all the common metals except mercury, silver, copper, and lead, hydrochloric acid produces hydrogen. The equation for the reaction with zinc is:

$$\underset{\text{zinc}}{Zn} + \underset{\text{hydrochloric acid}}{2\,HCl} \longrightarrow \underset{\text{zinc chloride}}{ZnCl_2} + \underset{\text{hydrogen}}{H_2\uparrow}$$

This reaction is exactly the same as that of the dry hydrogen chloride except that it takes place very rapidly and at room temperature.

123. Acids in general. Hydrochloric acid is an example of the large class of substances known as **acids,** all of which contain hydrogen. In a dilute water solution, the hydrogen can be liberated by metals, the action being a case of replacement. Some substances, like sugar, contain hydrogen, which cannot be replaced by metals; they are therefore not acids.

Water solutions of all acids have a peculiar sour taste, and all turn a certain natural dye, called litmus, from ***blue to red.*** Some of the commoner acids, beside hydrochloric and sulfuric, are nitric, acetic (which gives vinegar its sour taste), and citric acid (which is one of the acids present in lemons).

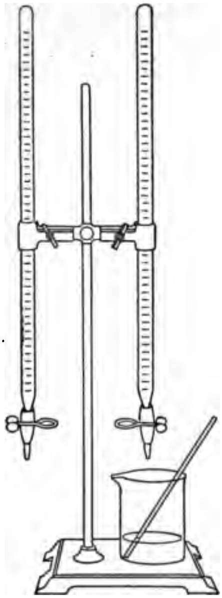

Fig. 76. Neutralization of an acid by a base.

Another characteristic of acids is their rapid reaction with certain compounds known as *bases.*

124. Bases. We saw (§ 31) that when sodium reacts with water, hydrogen and a compound called sodium hydroxide (NaOH) are formed. This compound is soluble in water and when its water solution is evaporated it is left as a white solid. Sodium hydroxide, known commercially as " caustic soda," is a typical base. Certain soluble bases (NaOH and KOH) are called **alkalies.** *Water solutions of bases have a peculiar biting, or caustic, taste and a soapy feeling. They change* ***red litmus to blue,*** which is the reverse of the change caused by acids. They all contain oxygen and hydrogen, a combination of atoms called the **hydroxyl group (OH).**

125. Neutralization of base and acid. When a base and an acid are brought together in solution in just the right proportion, the characteristic properties of each disappear. It is evident that there has been a chemical change. The base and the acid are said to neutralize each other, and the process is called **neutralization.** To determine just when the right amount of acid has been used to neutralize a given amount of base, we use litmus or some other **indicator** * like phenolphthalein.

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* An indicator is a substance which shows one color in an acid and another in a base solution.

If we allow 10 cc. of hydrochloric acid to run from a burette (Fig. 76) into a beaker, and add a drop or two of litmus, the solution becomes bright red. A dilute solution of sodium hydroxide is now added little by little from the other burette, and the solution is stirred. When a certain amount of the base has run in, the color of the solution suddenly turns blue. This shows that slightly too much base has been added. A few drops of acid will restore the red color, and a few drops more of the base will again make the solution blue. When the solution is at a point where a drop of either acid or base will reverse the process, the right proportions of acid and base are present. This is called the **end point**. Burettes are used in such an experiment so that the amount of acid and base employed may be accurately measured. If the solution is now evaporated, little cubes of a white solid will be found which is common salt.

By the reaction of sodium hydroxide and hydrochloric acid sodium chloride and water have been formed. The sodium chloride is soluble in water and can be found only by evaporation. The equation for this important reaction is:

$$\underset{\text{sodium hydroxide}}{\overset{\text{BASE}}{NaOH}} + \underset{\text{hydrochloric acid}}{\overset{\text{ACID}}{HCl}} \longrightarrow \underset{\text{sodium chloride}}{\overset{\text{SALT}}{NaCl}} + \underset{\text{water}}{\overset{\text{WATER}}{H_2O}}$$

Sodium chloride (common salt) is an example of a very large and important group of compounds known as **salts**. The process of neutralization always produces a salt and water. It should be noted that the metal of the base and the non-hydrogen part of the acid are united in the salt. *The compounds formed by the replacement of the hydrogen of an acid by a metal are called salts.*

126. Chlorides. The compound resulting from the union of an element and chlorine is called a **chloride**. All the salts which are formed from hydrochloric acid are called chlorides, irrespective of the base employed. Whenever a metal, such as zinc, reacts with hydrochloric acid, the metallic chloride (as zinc chloride) is made. Sometimes a chloride is formed by the direct combination of an element and chlorine, as, for instance, antimony and chlorine (§ 315).

All the common chlorides are readily soluble in water except those of silver (*$AgCl$*), *lead* (*$PbCl_2$*), *and mercury* (*$HgCl$*).

127. Test for a chloride. A solution of silver nitrate ($AgNO_3$) — which is made from silver and nitric acid — is a **test for a chloride,** because it produces a white, curdy precipitate ($AgCl$) with every solution which contains a chloride. A **precipitate** is an insoluble solid which results from a chemical action in solution.

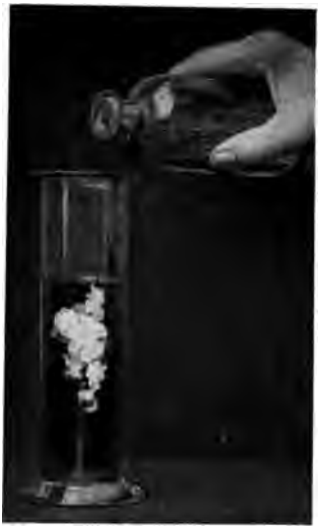


Fig. 77. Pouring silver nitrate into sodium chloride precipitates silver chloride.

If we dissolve a pinch of sodium chloride ($NaCl$) in water and add a few drops of silver nitrate solution, a white curdy precipitate (Fig. 77) consisting of silver chloride is at once produced. We may divide the liquid containing the precipitate into two parts and add ammonia water to one and nitric acid to the other. It will be seen that the precipitate dissolves in ammonia water and does not dissolve in nitric acid. It will also be observed that the *white precipitate turns purple on standing in the sunlight.*

The equation for this double decomposition is

$$\underset{\text{sodium chloride}}{NaCl} + \underset{\text{silver nitrate}}{AgNO_3} \longrightarrow \underset{\text{silver chloride}}{AgCl\downarrow} + \underset{\text{sodium nitrate}}{NaNO_3}$$

NOTE. The small arrow after AgCl pointing *downward* indicates that the silver chloride is precipitated and drops *down.*

This test is a very sensitive one, and the presence of a very minute quantity of chloride can thus be recognized.

128. Uses of hydrochloric acid. Very small quantities of hydrochloric acid are always found in the stomach, for its presence is necessary in the digestive process. This acid is produced in the body from the salt that is taken with the food.

Concentrated hydrochloric acid is manufactured in considerable quantities for use in the industries and in laboratories. It is generally shipped in large glass carboys (Fig. 78) packed in wooden boxes. It is used by tinmen and plumbers for cleaning metal surfaces which are to be soldered.

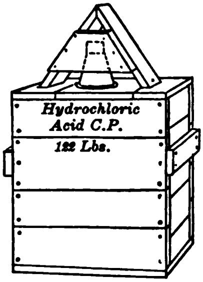

Hydrochloric
Acid C.P.
122 Lbs.

Fig. 78. Carboy of acid packed for transportation.

129. Composition of hydrogen chloride. The fact that hydrogen chloride is composed of hydrogen and chlorine may be demonstrated in the same way that the composition of water is shown; that is, by electrolysis.

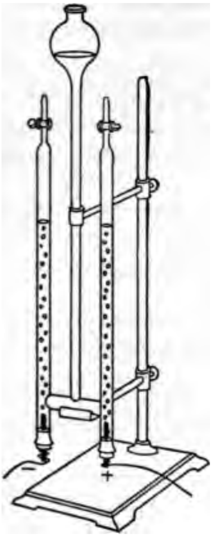


Fig. 79. Electrolysis of hydrochloric acid.

If concentrated hydrochloric acid is placed in the apparatus (Fig. 79) and an electric current is passed through the solution, we find that hydrogen is produced at the negative (−) electrode and chlorine at the positive (+). At first the gases collect at unequal rates because the chlorine dissolves in the solution; but after a time the liquid becomes saturated, and both gases, the hydrogen and the chlorine, collect in the tubes in equal volumes.

In this experiment we obtain from the aqueous solution of hydrogen chloride equal volumes of hydrogen and of chlorine, a gas which we have not as yet considered. This new gas is found to be greenish in color and to have a suffocating and irritating effect when breathed into the lungs.

We may also, as in the case of water, reverse the experiment and *show the formation of hydrogen chloride by the synthesis of equal volumes of hydrogen and chlorine.*

A small bottle (Fig. 80) is filled with concentrated hydrochloric acid nearly up to the neck, and an electric current is sent through the solution for about 15 minutes. We then connect the exit tube with a stout glass tube (Fig. 81) which has a stopcock at each end. We allow the gases, hydrogen and chlorine, to pass through the straight tube and then to bubble through a sodium hydroxide solution. The whole apparatus has been covered with a dark cloth to prevent a premature explosion due to the sunlight. It is best to let the gases pass through the apparatus for at least 15 minutes more, then to close both cocks and to stop the current.

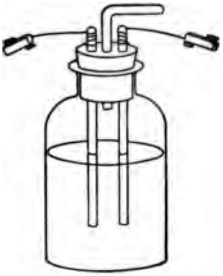


Fig. 80. Preparation of hydrogen and chlorine.

The mixture of hydrogen and chlorine may be exploded by an electric spark if the tube is provided with platinum wires; or it may be exploded still more easily by exposure to direct sunlight or to a magnesium flashlight. Caution! The gases explode instantly, but there is no noise, only a little click with a flash of light in the tube.

To show the volume of hydrogen chloride gas formed, we may place one end of the tube under some mercury in a dish and open the stopcock at that end. Since the mercury does not rise in the tube and no bubbles of gas escape, *the volume of the hydrogen chloride is just equal to the sum of the volumes of hydrogen and chlorine.*

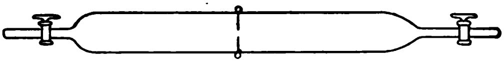


Fig. 81. Tube for synthesis of hydrogen chloride.

If we now open one end of the tube beneath water, we notice that the water is sucked up into the tube with a rush. On testing the water in the tube we find that it is hydrochloric acid.

These experiments show that *one volume of hydrogen combines with one volume of chlorine to form two volumes of hydrogen chloride gas.*

$$\boxed{H_2} \quad + \quad \boxed{Cl_2} \quad \longrightarrow \quad \boxed{HCl \mid HCl}$$

1 vol. hydrogen + 1 vol. chlorine → 2 vol. hydrogen chloride

This is a very interesting illustration of Gay-Lussac's Law of Volumes (§ 58).

SUMMARY OF CHAPTER XII

HYDROGEN CHLORIDE IS PREPARED by the action of concentrated sulfuric acid on sodium chloride.

PROPERTIES: Hydrogen chloride is a colorless gas with a pungent odor. It forms a cloud with moist air, is extremely soluble in water, and is one-fourth heavier than air. The dry gas is inactive.

HYDROCHLORIC ACID (or muriatic acid) is a water solution of hydrogen chloride. It is a *typical acid:* it reacts with metals, such as zinc, evolving hydrogen; it tastes sour and turns blue litmus red.

A CHLORIDE is a compound of chlorine and some other element. All the common chlorides except three are soluble in water.

BASES are compounds which will *neutralize* acids. They are mostly hydroxides of metals. Those that are soluble in water are *alkaline;* they turn red litmus blue.

SALTS are the compounds produced by the replacement of the hydrogen of an acid by a metal. A salt and water are produced by the neutralization of a base by an acid.

COMPOSITION OF HYDROGEN CHLORIDE: one volume of hydrogen will combine with one volume of chlorine to yield two volumes of hydrogen chloride.

QUESTIONS AND PROBLEMS

1. In preparing hydrogen chloride, what substance furnishes the hydrogen? what substance the chlorine?

2. Why is the aqueous solution of hydrogen chloride more useful than the dry gas?

3. What are the three characteristic properties of acids in water solutions?

4. How does a base differ from an acid?

5. How would you prove that a given solution contained a chloride?

6. What are the products formed in neutralizing a base with an acid?

7. Why does a *tinman* use muriatic acid in soldering metals?

8. Why is hydrochloric acid not shipped in tin cans?

9. What are the difficulties in connection with the electrolysis of hydrochloric acid?

10. What precautions must be taken in the synthesis of hydrogen chloride?

11. What chemical law is illustrated in the synthesis of hydrogen chloride? What other experiment have we had which illustrates the same law?

12. Calculate the percentage composition of hydrogen chloride.

13. How many grams of sodium chloride are needed to yield, with sulfuric acid, 30 grams of hydrogen chloride?

14. If the gas in Problem 13 is dissolved in water, making a 30% solution whose density is 1.15 grams per cubic centimeter, how many cubic centimeters of hydrochloric acid will be produced?

REVIEW QUESTIONS

1. Define and explain the terms *element; compound; atom; molecule.*

2. (*a*) Define an *acid*, a *base*, and a *salt.* (*b*) Write equations illustrating methods for making one member of each of these classes of substances.

3. What weight of sodium sulfate could be obtained from 10 grams of sodium chloride ?

4. State the Law of Multiple Proportions. Explain this law by means of examples.

5. Write the following equations in complete form, using formulas:

(Hot) copper and oxygen (gas) = ?
(Hot) zinc and water (vapor) = ?
Zinc oxide and sulfuric acid = ?
Magnesium and hydrochloric acid = ?
Sodium hydroxide and sulfuric acid = ?

TOPIC FOR FURTHER STUDY

The manufacture of hydrochloric acid. What is the commercial method of preparing hydrochloric acid? What raw materials are used? What is the by-product? Of what is the apparatus built? Why? Consult a book on Industrial Chemistry (*Thorp's* or *Rogers'*).

CHAPTER XIII

ATOMIC AND MOLECULAR WEIGHTS *

Formula is result of experiments — Avogadro's theory — its consequences — hydrogen molecule has two atoms — problems involving volumes of gases only — molecular weights — gram-molecular volume — atomic weights — atomic weight from molecular weight — combining weights — precise determination of atomic weights — finding the formula of a compound.

130. A formula is the result of experiments. Thus far we have shown no experimental evidence why the molecules of hydrogen, oxygen, nitrogen, and chlorine should be represented by H_2, O_2, N_2, and Cl_2. Nor have we attempted to explain why a molecule of water is represented by H_2O, a molecule of sulfuric acid by H_2SO_4, and a molecule of acetylene gas by C_2H_2. This interesting problem of how the formula of a substance is determined by experiment we shall discuss in this chapter.

131. Uniformity of gases. We have already learned in Chapter V that all gases behave alike as regards the effects of pressure. Thus, *the volume of any gas varies inversely as the pressure if the temperature remains the same,* according to BOYLE'S LAW. We have also learned that all gases behave alike as regards the effects of temperature. Thus, *the volume of any gas varies directly as the absolute temperature if the pressure remains the same,* according to the LAW OF CHARLES.

In Chapter VI we learned from the volumetric synthesis of steam that

$$\textbf{2 vol. hydrogen} + \textbf{1 vol. oxygen} \longrightarrow \textbf{2 vol. steam}$$

---

* Some teachers may prefer to postpone or omit this chapter.

In Chapter XII we have just seen that

1 vol. hydrogen + 1 vol. chlorine ⟶ 2 vol. hydrogen chloride

A careful study of the process of making ammonia gas by the direct union of hydrogen and nitrogen gives these results:

3 vol. hydrogen + 1 vol. nitrogen ⟶ 2 vol. ammonia

These experimental facts all illustrate the LAW OF GAY-LUSSAC:

The volumes of gases used and produced in a chemical change can always be represented by the ratio of small whole numbers.

132. Avogadro's explanation. These striking cases of uniformity in the behavior of gases led the famous Italian, Avogadro (Fig. 82), in 1811 to the following explanation: He assumed that *equal volumes of gases under like conditions of temperature and pressure contain the same number of molecules.* In other words, 1 cubic centimeter of hydrogen has just as many molecules as 1 cubic centimeter of oxygen, nitrogen, chlorine, hydrogen chloride, or any other gas, provided the conditions of temperature and pressure are the same.

FIG. 82. PORTRAIT MEDAL OF AMEDEO AVOGADRO (1776–1856).
Professor of physics at Turin, Italy.

133. Consequences of this theory. It should be noticed at once that this theory makes no assumption as to the *actual* number of molecules in a cubic centimeter. But it does give us a simple method of comparing the weights of molecules of gas by comparing the densities of the gases, that is, their weights per unit volume. We can best show this in a table:

Gas	Density (Grams per liter)	Relative Weights of Molecules
Hydrogen	0.09	1
Oxygen	1.43	16
Nitrogen	1.25	14
Hydrogen chloride	1.64	18.2

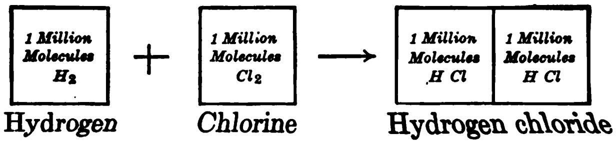
In this table we have used only the approximate values for densities and have taken hydrogen as the basis of comparison. It will be seen that the third column gives us the relative weights of the molecules referred to the hydrogen molecule as a standard.

134. Hydrogen molecule has two atoms. Another very interesting conclusion that we draw from Avogadro's theory is that *every molecule of hydrogen has at least two atoms.* Let us see why this is so. Our experiment in the synthesis of hydrogen chloride showed that

1 vol. hydrogen + 1 vol. chlorine ⟶ 2 vol. hydrogen chloride

According to Avogadro we must assume that we have the same number of molecules of hydrogen as of chlorine and *twice* that number of molecules of hydrogen chloride. Suppose we have a million molecules of hydrogen; then we must have a million molecules of chlorine and *two* million molecules of hydrogen chloride. Each one of these molecules of hydrogen chloride must contain at least one atom of hydrogen; so that we have in all *two million* **atoms** of hydrogen coming from *one million* **molecules** of hydrogen. This experiment indicates that **each molecule of hydrogen contains at least 2 atoms of hydrogen.**

It may help us to picture this relation if we draw squares to represent the equal volumes, as shown below:


1 Million Molecules H_2
+
1 Million Molecules Cl_2
⟶
1 Million Molecules $H Cl$
1 Million Molecules $H Cl$
Hydrogen
Chlorine
Hydrogen chloride

By a similar course of reasoning it follows that the chlorine molecule also contains at least two atoms.

We represent these facts by the following equation:

$$H_2 + Cl_2 \longrightarrow 2\,HCl$$

This means that one molecule of hydrogen, containing 2 atoms, plus one molecule of chlorine, containing 2 atoms, gives 2 molecules of hydrogen chloride, each containing one atom of hydrogen and one atom of chlorine.

NOTE. It should be remembered that any *even* number might be used instead of two; but since there is no reaction in which the hydrogen molecule appears to be divided into more than two parts, we decide that there must be *only* two atoms in the molecule.

From a consideration of the volumetric synthesis of steam, we come by similar reasoning to the conclusion that the oxygen molecule contains two atoms; and from a study of the synthesis of ammonia, we conclude that the nitrogen molecule also contains two atoms.

135. Problems involving volumes of gases. One of the practical advantages which results from writing our equations involving the reaction of gases *in molecular form* is that it gives us a very simple method of computing the volumes of the gases involved.

FOR EXAMPLE, suppose we wish to find the volume of oxygen needed to burn 1 liter of carbon monoxide.

We first write the equation

$$2\,CO + O_2 \longrightarrow 2\,CO_2$$

Since equal numbers of molecules of gases occupy equal volumes, we may read the equation thus:

$$2 \text{ vol. } CO + 1 \text{ vol. } O_2 \longrightarrow 2 \text{ vol. } CO_2$$

Therefore 1 liter of CO will require one-half a liter or **500** cc. of oxygen.

RULE. *In the case of gases the coefficients of formulas in equations represent the relative volumes of the substances.*

136. Finding molecular weights. We have just seen how, by comparing the densities of gases, we may get the relative weights of their molecules. But the chemist takes as his standard the **hydrogen atom.** Therefore, *the molecular weight of a substance is a number which expresses how many times its molecule is heavier than the hydrogen atom.*

For example, the density of oxygen is approximately 1.43 grams per liter, and the density of hydrogen is about 0.09 grams per liter; therefore the density of oxygen is $\frac{1.43}{0.09}$ or about 16 times the density of hydrogen. According to Avogadro, these densities will have the same ratio as the weights of the molecules. Therefore one molecule of oxygen weighs 16 times as much as one molecule of hydrogen. But we have just seen that one molecule of hydrogen contains two atoms; therefore one molecule of oxygen weighs 2×16 or 32 times as much as one atom of hydrogen. In other words, **the molecular weight of oxygen is 32.**

In the same way we can find the molecular weight of nitrogen. Since nitrogen is 14 times as heavy as hydrogen, its molecule is 2×14 or 28 times as heavy as the hydrogen atom. Also, in comparing the densities of hydrogen chloride and hydrogen, we find that hydrogen chloride is 18.2 times as heavy as hydrogen, and therefore its molecular weight is 2×18.2 or 36.4.

137. Gram-molecular volume. We have just seen that the molecular weight of oxygen is 32. The chemist often has occasion to use as many grams of a gas as there are units in its molecular weight, and so he calls this weight the **gram-molecular weight.** Thus, 32 grams is the gram-molecular weight of oxygen, 28 grams is the gram-molecular weight of nitrogen, and 36.4 grams is the gram-molecular weight of hydrogen chloride.

What volume does 32 grams of oxygen occupy under standard conditions? Since one liter of oxygen weighs approximately 1.43 grams, it follows that it takes $\frac{32}{1.43}$ or **22.4** liters of oxygen to weigh 32 grams. If we divide the gram-mole weight of *any gas* by its density, we always get 22.4 li Therefore we conclude that *the gram-molecular weight of gas occupies a volume of liters.*

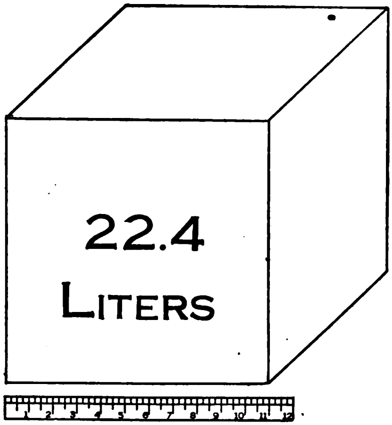


Fig. 83. Cube representing one gram-molecular volume.

This gaseous volum 22.4 liters (Fig. 83) is of great importance to chemist in the labora for it furnishes him a c means of calculating molecular weight of any stance which can be wei in the gaseous state: a has to do is to compute the weight of a given ume under standard c tions what 22.4 liters w weigh in grams.

FOR EXAMPLE, carbon dioxide weighs approximately 1.98 g per liter; therefore 22.4 liters would weigh 22.4×1.98 or abo grams. The molecular weight of carbon dioxide is, then, ap mately 44.

Again, nitrogen weighs 1.25 grams per liter; therefore 22.4 would weigh 22.4×1.25 or about 28 grams. The molecular w of nitrogen is, then, approximately 28.

QUESTIONS AND PROBLEMS

1. State the facts and theories which lead us to believe tha oxygen molecule contains two atoms.

2. State approximately the relative number of molecules of nit and oxygen in the atmosphere.

3. From the table of densities of gases given in the App compute the molecular weights of the following gases: (*a*) Acety

(*b*) Ammonia; (*c*) Carbon monoxide; (*d*) Hydrogen sulfide; and (*e*) Sulfur dioxide.

4. The equation for the reduction of carbon dioxide with red-hot carbon is as follows:

$$CO_2 + C \longrightarrow 2\,CO$$

and the equation for burning carbon monoxide is:

$$2\,CO + O_2 \longrightarrow 2\,CO_2$$

(*a*) What volume of carbon monoxide will be produced by the reduction of 100 liters of carbon dioxide?

(*b*) What volume of oxygen is needed to burn the carbon monoxide produced in problem (*a*)?

5. When 150 cc. of hydrogen burn in chlorine, how many cubic centimeters of hydrogen chloride are produced?

6. If the molecular weight of nitrous oxide is 44, what is the approximate density (grams per liter) of the gas?

7. The density of helium is 0.178 grams per liter and its atomic weight is 3.99. How many atoms does a helium molecule contain?

138. Atomic weights. Another result of Avogadro's theory is that it gives us a direct method of calculating the relative weights of the atoms, that is, the atomic weights. We have just seen that the oxygen molecule is approximately 16 times as heavy as the hydrogen molecule, and we have also seen that the oxygen and hydrogen molecules each have 2 atoms. Therefore we can say that the oxygen atom is 16 times as heavy as the hydrogen atom; in other words, *the atomic weight of oxygen is 16, referred to the hydrogen atom as a standard.*

In the same way we can compute the atomic weight of nitrogen as 14 and of chlorine as 35.5.

Unfortunately we cannot apply this same method to all the elements because we cannot obtain them in the gaseous condition.

139. Atomic weight from molecular weight. We have seen that the molecular weight of a substance expresses the number of times its molecule is heavier than the hydrogen atom; and that the *atomic weight of* a substance expresses the number of times its atom is heavier than the hydrogen atom, the unit in each case being the same, namely, the hydrogen atom. It is evident, then, that the molecular weight of a compound is equal to the sum of the atomic weights of its constituent atoms.

It is possible experimentally (by means of its density, if it is a gas, and also by other methods not described here) to determine the molecular weight of a compound; it is also possible to determine experimentally its percentage composition by weight. If, then, *we multiply the molecular weight of the compound by the percentage of each element present, we shall get numbers which are the atomic weights, or some multiple of them, of the constituent elements.* Further, if we analyze several compounds of the same element, we shall find that the numbers obtained by multiplying the molecular weights by the percentage composition of the element will in each case be the same, or multiples. We then take as the atomic weight the smallest weight of any given element in the compounds considered. In other words, by this method *the smallest weight of an element found in the gram-molecular weights of its compounds is the atomic weight of that element.*

FOR EXAMPLE, let us determine the atomic weight of the element carbon. This element forms a number of gaseous compounds, whose molecular weights can easily be determined by finding the densities and multiplying by 22.4 (§ 137). The molecular weights of four such gaseous compounds of carbon (carbon dioxide, carbon monoxide, marsh gas, and acetylene) are given in the following table. We determine by experiment the percentage of carbon in each of these gases; the results are given in the third column. If we now, in each

NAME OF GAS	MOLECULAR WEIGHT (22.4 l.)	PERCENTAGE OF CARBON BY EXPERIMENT	PART OF MOLECULAR WEIGHT DUE TO CARBON
Carbon dioxide . .	44.28	27.27	12.08
Carbon monoxide .	28.02	42.86	12.01
Marsh gas . . .	16.06	75.0	12.08
Acetylene	25.98	92.31	23.98

case, multiply the molecular weight by the percentage of carbon, we shall find what part of the molecular weight is due to the carbon (fourth column).

From the results in the fourth column it is evident that "the smallest weight of this element found in the gram-molecular weights of its compounds" is 12. Therefore *the atomic weight of carbon is approximately 12.* No compound has ever been found which gives a smaller weight for carbon.

140. Atomic weights and combining weights. If we analyze hydrogen chloride we shall find that 35.5 grams of chlorine are united with 1 gram of hydrogen. The chemist calls this number 35.5 the **combining weight** or **reacting weight** of chlorine. *The combining, or reacting, weight of an element is the weight of that element which combines with or replaces 1 gram of hydrogen.* It will be seen at once that this combining weight is exactly equal to the atomic weight of chlorine, which we have already determined by comparing the densities of the elementary gases chlorine and hydrogen. Indeed, this combining weight *must* be its atomic weight, because a molecule of hydrogen chloride (HCl) consists of but one atom of hydrogen combined with one atom of chlorine.

Unfortunately the combining weights of some elements are *not* equal to their atomic weights. If we analyze water (§ 59) we find that 1 part of hydrogen unites with 8 parts by weight of oxygen, and therefore the combining weight of oxygen is 8, or *one-half its atomic weight.* It has been found in general that *the atomic weight of an element is equal to its combining weight or some multiple of it.* In the case of oxygen this multiple is 2.

Let us take the case of an element which does not combine with hydrogen but which replaces it. Such an element is sodium; its combining weight may be determined as follows:

If we put metallic sodium in water, hydrogen and sodium hydroxide are formed. When this experiment is done quantitatively, we find that 23 grams of sodium replace 1 gram of hydrogen. Therefore the combining weight of sodium is 23.

141. An indirect method of determining the combining weight. The question might easily arise, How can we determine the combining weight of an element which does not combine with or replace hydrogen? If we analyze black copper oxide, we find that 31.8 grams of copper are combined with 8.00 grams of oxygen. That is, the combining weight of oxygen (8.00 grams) is united to 31.8 grams of copper; hence we feel sure that if copper and hydrogen did unite, 31.8 grams of copper would combine with 1 gram of hydrogen. The combining weight of copper is therefore 31.8.

In general, *when an element does not unite with or replace hydrogen, we can determine its combining, or reacting, weight by finding what weight of it will unite with the known combining weight of another element.*

142. Precise determination of atomic weights. The combining, or reacting, weight of an element can be determined in the laboratory with great accuracy. The method for determining atomic weights which has already been described (§ 139) involves finding the density of a gas. This cannot be done with exactness, and therefore the results are only approximate. To find the precise atomic weight we determine the combining, or reacting, weight with great care and then multiply by some small whole number which will make the result agree with the approximate value.

Up to this point we have assumed that the oxygen atom was exactly 16 times as heavy as the hydrogen atom. Precise experiments have shown, however, that oxygen is 15.901 times as heavy as hydrogen, so that the atomic weight of oxygen, on the basis that hydrogen is 1, would be 15.901. For many reasons chemists have found it more convenient to call the *atomic weight of oxygen exactly 16.00*, which makes the atomic weight of hydrogen 1.008.

These values for atomic weights are thus, obviously, dependent on the precise chemical analysis of compounds. Such experimental work must be done with extreme care and extraordinary precision. One of the first chemists to make a systematic study of atomic weights was Berzelius. His methods have been greatly improved upon by later chemists, and today the accepted atomic weights are the result of very elaborate experiments. Theodore W. Richards (Fig. 84) is the foremost modern chemist in this field of investigation.

FIG. 84. THEODORE W. RICHARDS (1868–).

Professor of chemistry at Harvard University. Awarded Nobel prize in 1915 for his work on atomic weights.

143. Necessary steps in an atomic weight determination. We may now summarize the necessary steps in determining the atomic weight of an element.

First, Find the approximate atomic weight. To do this, (*a*) determine the molecular weights of a number of gaseous compounds by finding their density; (*b*) determine the percentage of the element in each of these compounds by carefully analyzing them; (*c*) find what part of the molecular weight is due to the element by multiplying the molecular weight of the compound by the percentage of the element in it; (*d*) note the smallest weight of the element which is found in the gram-molecular weight of these compounds.

Second, Determine very accurately the combining weight of the element in one or more compounds.

Third, Multiply the combining weight by some small whole number (1, 2, or 3) which will give a result close to the approximate atomic weight. The number thus obtained will be the *precise atomic weight.*

144. Determining the formula of a compound. To find the precise value of atomic weights requires very great technical skill and patience. *For us the main thing is to learn to use atomic weights.*

One very important use of atomic weights is in finding the formula of a compound. We shall now illustrate this by determining the formulas of water, sulfuric acid, and acetylene.

Water. We find that its percentage composition is as follows: hydrogen 11.19 per cent, and oxygen 88.81 per cent. By experiment we also find that its molecular weight is approximately 18. Then the solution is as follows:

	Percentage composition		Atomic weight		Atomic ratio
Hydrogen . . .	11.19	÷	1	=	11.2
Oxygen	88.81	÷	16	=	5.55

Dividing the percentages (by weight) by the atomic weights gives as quotients numbers which show the relative number of each kind of atom. If we assume that there is one atom of oxygen in the molecule, then there must be 2 atoms of hydrogen. In other words, divide the several quotients in column three by the smallest one of them. (That is, $11.2 \div 5.55 = 2.$) Therefore the simplest formula for water is H_2O. This gives a molecular weight of $2 + 16$ or 18, which corresponds with the experimental value given.

Sulfuric Acid. Given the percentage composition: hydrogen 2.04 per cent, sulfur 32.65 per cent, and oxygen 65.31 per cent.

	Percentage composition		Atomic weight		Atomic ratio
Hydrogen . . .	2.04	÷	1	=	2.04
Sulfur	32.65	÷	32	=	1.02
Oxygen	65.31	÷	16	=	4.08

These quotients are evidently in the same ratio as the number of atoms of each element in the molecule. That is, there are 2 atoms of hydrogen ($2.04 \div 1.02$), 1 atom of sulfur ($1.02 \div 1.02$), and 4 atoms of oxygen

(4.08 ÷ 1.02); and the simplest formula of sulfuric acid is H_2SO_4. In this case the molecular weight is very difficult to obtain, and so we accept the simplest formula.

Acetylene. Suppose we have given that the gram-molecular weight of acetylene is 25.98, that it contains 92.31 per cent carbon, and that the rest is hydrogen. To find the formula of acetylene the solution may be arranged thus:

	Percentage composition		Atomic weight		Atomic ratio
Carbon	92.3	÷	12	=	7.7
Hydrogen . . .	7.7	÷	1	=	7.7

The simplest formula would be CH, but then the molecular weight of CH would be 13. Hence, in order to get the experimental value 25.98, the formula must be *doubled*. Therefore the formula for acetylene is C_2H_2.

SUMMARY OF CHAPTER XIII

UNIFORM BEHAVIOR OF ALL GASES:

The volume of any gas varies inversely as the pressure if the temperature remains the same (Boyle's Law).

The volume of any gas varies directly as the absolute temperature if the pressure remains the same (Law of Charles).

The volumes of gases used and produced in a chemical change can always be represented by the ratio of small whole numbers (Law of Gay-Lussac).

AVOGADRO'S THEORY: Equal volumes of gases under the same conditions of temperature and pressure contain the same number of molecules.

As a *consequence* of this theory, we conclude that molecules of hydrogen, oxygen, nitrogen, and chlorine have *two* atoms each.

RELATIVE VOLUMES OF GASES are represented by the coefficients of their molecules in an equation.

MOLECULAR WEIGHT of a substance is the number which expresses how many times its molecule is heavier than the hydrogen atom.

Gram-molecular weight **of any gas occupies a volume of 22.4 liters.**

ATOMIC WEIGHT of an element is a number which expresses the relative heaviness of its atom. Atomic weight of oxygen, 16, is taken as the standard.

Atomic weight **of an element is** ***determined*** **approximately by getting the number representing the smallest weight of the element in the gram-molecular weight of any of its compounds.**

COMBINING, OR REACTING, WEIGHT of an element is the weight of that element in grams which combines with or replaces 1 gram (more exactly 1.008 grams) of hydrogen.

ATOMIC WEIGHT is either equal to or a multiple of the ***combining weight.***

TO FIND THE FORMULA FROM PERCENTAGE COMPOSITION: Divide the percentage of each element by its atomic weight; the quotients will be the relative number of each kind of atom. Use molecular weight to find what multiple of the simplest formula to use.

PROBLEMS

1. If 500 cc. of marsh gas under standard conditions weighs 0.36 grams, what is the molecular weight of marsh gas?

2. If the marsh gas in Problem 1 is composed of 75% carbon and 25% hydrogen, how many atoms of each element does one molecule of the compound contain? (Assume the atomic weights as given on the back cover.)

3. A certain gas contains 30.4% nitrogen and 69.6% oxygen. What is the simplest formula which could be used to express its composition?

4. The analysis of a substance showed carbon 80% and hydrogen 20%. The molecular weight was found to be 30. What is its formula?

5. When a liquid is heated to 150° C., it is found that 185 cc. of the gas formed weighs 0.247 grams. What is its gram-molecular weight?

6. The quantitative analysis of the liquid used in Problem 5 showed hydrogen 13.0%, oxygen 34.8%, and carbon 52.2%. Calculate its formula.

7. Given the formula of carbon monoxide as CO; compute its density (grams per liter) under standard conditions.

8. When marsh gas burns the equation for the reaction is as follows:

$$CH_4 + 2\,O_2 \longrightarrow CO_2 + 2\,H_2O$$

(*a*) Calculate the volume of oxygen used when 1000 cubic feet of this gas burns. (*b*) Calculate the volume of air used in burning the same volume of gas. (*c*) Calculate the volume of carbon dioxide formed.

9. The analysis of a certain compound showed: hydrogen 0.84%; carbon 10.05%; and chlorine 89.11%. What would be the simplest formula which represents this composition?

10. To determine the molecular weight of the compound used in Problem 9, an experiment was performed which showed that 0.250 g. of the substance gave 53.0 cc. of gas when collected over water at 20° C. and 740 mm. Calculate the gram-molecular weight of the substance, and revise your answer in Problem 9 accordingly.

11. The analysis of ammonia gas shows that it is 82.4% nitrogen, and the remainder is hydrogen. Compute the combining weight of nitrogen.

12. From a study of the following data in regard to nitrogen compounds and from the combining weights found in the previous problem, calculate the atomic weight of nitrogen:

NITROGEN COMPOUNDS	DENSITY (grams per liter)	PER CENT OF NITROGEN
Ammonia	0.762	82.4
Nitrous oxide	1.97	63.6
Nitric oxide	1.34	46.7

TOPIC FOR FURTHER STUDY

The exact determination of atomic weights. The modern methods of atomic weight determination involve many experimental precautions; the fundamental chemical facts are, however, very simple. Consult the work of Morley on hydrogen and oxygen (Smithsonian Contributions, No. 980) and Richards on chlorine and silver (Carnegie Publication 69).

CHAPTER XIV

VALENCE AND NOMENCLATURE

Why valence is important — its meaning — graphical representation — valence of common elements and groups — variations in valence — its use in writing formulas — rule — replacement reactions — relation of atomic and combining weights to valence.

Naming compounds — bases — acids — salts.

145. Importance of valence. A knowledge of valences and an ability to use them are of great help in the study of chemistry. For instance, they will aid us in writing the formulas of compounds: if we know the valences of two elements we can predict the formula of their compound (if they combine), even before we have determined its composition and formula experimentally. Likewise, if we know the composition of one compound of two elements, we can predict the formulas of many other compounds involving these elements. Thus, knowing the composition of thorium oxide to be ThO_2, we can predict that of thorium sulfate, thorium chloride, thorium nitrate, etc.

146. What do we mean by valence? In our study of compounds we have noticed that the various elements differ greatly from one another in the number of hydrogen atoms with which they will combine. This fact is illustrated in these compounds:

HCl	H_2O	NH_3	CH_4
hydrogen chloride	**water**	**ammonia**	**marsh gas**

Thus, an atom of chlorine will combine with *but one* hydrogen atom, an atom of oxygen with *two*, an atom of nitrogen with *three*, and an atom of carbon with *four*. We call this ***property of an element which determines the number of hydrogen atoms that its atom can hold in combination or can replace its valence.*** In other words, the valence of chlorine is one, of oxygen two, of nitrogen three, and of carbon four.

147. Graphical representation. The valences of elements do not tell us anything about the reasons why certain elements unite and certain others do not. They merely tell us with how many hydrogen atoms elements can combine. Furthermore we do not know in what way the elements are actually joined to one another; but our rules of valence tell us how many atoms will be united in a given compound. We can picture this graphically by supposing that each atom has a certain number of hooks, or **bonds**, which enable it to join to some other atom or atoms. We are quite certain, of course, that the actual way in which atoms are linked is different from that represented by rigid hooks, but we may use this method in order to visualize the conception of valence.

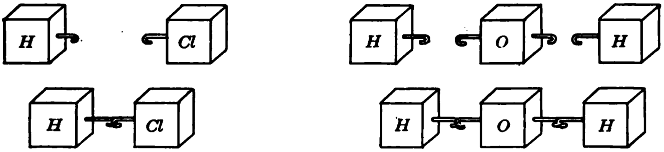


Fig. 85. Diagram representing the valence of atoms by hooks.

The accompanying diagrams (Fig. 85) represent such an imaginary linkage of the atoms in hydrogen chloride and water. It is obvious that if elements unite with one atom of hydrogen they must have only one bond, or hook; their valence is one. Similarly, elements which combine with two, three, and four atoms of hydrogen have two, three, and four bonds respectively. If an element like zinc, which has a valence of two, unites with chlorine, which has a valence of one, it will require two chlorine atoms to link up with the two bonds of a single zinc atom. The formula will, therefore, be $ZnCl_2$.

148. Valences of common elements and groups. We may indicate the valence of an element or a group of elements by writing slightly above and to the right of the symbol a small Roman numeral, thus: H^{I}, O^{II}, N^{III}, C^{IV}. Because hydrogen has only one bond, we take it as our standard of valence.

Using this system for indicating the valence of an atom, we show in the following table the valences of the common elements and of some common groups of elements. Certain groups of elements, like the hydroxyl (OH) group in bases and the SO_4 group in sulfuric acid, the NO_3 group in nitric acid and the NH_4 group in ammonium compounds, remain intact throughout a number of reactions. Such groups of elements act very much like a single element and are called **radicals.** Radicals have valences just as do elements. Elements or groups which have the valence of one are called monovalent; if they have a valence of two, divalent, etc.

Valences of Common Elements and Radicals

Monovalent	Divalent	Trivalent	Tetravalent
H	Ca	Al	Sn
Cl	Ba	Bi	C
Na	Mg	Sb	Si
K	Zn	Fe	S
Ag	Hg	P	SiO_4
NH_4	Cu	N	
OH	Fe	PO_4	Pentavalent
NO_3	Sn		
	S		N
	O		P
	SO_4		As
	CO_3		Sb

149. Variable valence. It will be noticed in the above table that certain elements are indicated as having more than one valence. Such facts complicate the general rules of valence. Almost all elements form a certain number of compounds in which they have an unusual valence. For example, the valence of carbon is almost without exception four, as in carbon dioxide (CO_2) (oxygen is divalent and there are two oxygen atoms). But in carbon monoxide (CO) the valence is two. Such exceptions are rare and must simply be learned as they occur. A few elements, like iron, form *two* series of compounds in which the element has different valences. For example, we have a number of compounds of iron called ferrous compounds, in which iron has a valence of *two;* others are called ferric compounds, in which iron has a valence of *three.* Such elements are said to have a variable valence.

150. Writing formulas. Let us now see how we can apply the information in the valence table to the writing of formulas. We shall first take a compound of aluminum and chlorine called aluminum chloride. We see from the above table that chlorine has a valence of one (Cl^{I}) and aluminum three (Al^{III}); therefore the formula must be $Al^{III}Cl^{I}_3$. Let us take another case: the compound formed by neutralizing calcium hydroxide with sulfuric acid is called calcium sulfate. The sulfate radical has a valence of two (SO_4^{II}), calcium also has a valence of two (Ca^{II}); therefore the formula is $Ca^{II}SO_4^{II}$. The two bonds of calcium are joined with the two bonds of the sulfate group.

Sodium sulfate, made by neutralizing sodium hydroxide and sulfuric acid, has the formula $Na^{I}_2SO_4^{II}$ since it requires two atoms of monovalent sodium to hook on to the two bonds of the sulfate radical. Aluminum sulfate has the formula $Al_2^{III}(SO_4^{II})_3$. Since the valence of aluminum is three, it is necessary to have two aluminum atoms (a total of six bonds) and three sulfate groups (a total of six bonds) linked up together in order to satisfy all the bonds of the aluminum and of the SO_4 radical in this compound. We must remember that *in writing formulas we have to take such a number of atoms of each element* (or of groups) *that all the bonds of both elements* (or groups) *will be united.*

In writing formulas of molecules made up of two atoms or radicals of unequal valence we shall find the following Rule for Valence helpful:

Valence × *number of atoms* (or radicals) in the case of one element (or radical) *equals valence* × *number of atoms* (or radicals) in the case of the other.

In the case of aluminum sulfate we have a valence of three and two, and we can satisfy these requirements only by having a total of six bonds. There is a radical in phosphoric acid which has the formula $-PO_4^{III}$ and a valence of three. Sodium phosphate will, therefore, have the formula Na_3PO_4 since we must take three atoms of the monovalent sodium. The aluminum compound will, however, have the formula $Al^{III}PO_4^{III}$ since aluminum is trivalent and so is the phosphate radical. The student will do well to practice writing formulas for a great variety of compounds based on the valences of the elements and radicals given in the tables.

It is very important to *learn the valence of each element or radical as we study it, and always to use it in writing formulas.* The student will find it good practice to check up every formula that he writes in order to make sure that the total valences of the two halves of the compound balance. It is not necessary to memorize the entire table of valences, provided he remembers the formula of at least one simple compound of each element. For example, suppose he wishes the valence of mercury. Perhaps he recalls that the formula of the red oxide of mercury is HgO^{II}. Then, since the valence of oxygen is two, the valence of mercury in this compound is also two.

151. Replacement reactions. When one element of a compound replaces another, the number of atoms of the elements concerned must be such that the valences of the replacing element must equal the valences of the element replaced. Thus, when zinc replaces hydrogen in hydrochloric acid, each atom of zinc replaces two atoms of hydrogen since the valence of zinc is two and the valence of hydrogen one:

$$Zn + 2\,HCl \longrightarrow ZnCl_2 + H_2$$

When aluminum reacts with hydrochloric acid, three atoms of hydrogen appear for every atom of aluminum since the valence of the metal is three:

$$2\,Al + 6\,HCl \longrightarrow 2\,AlCl_3 + 3\,H_2$$

This use of the rules of valence will be found helpful in writing replacement reactions.

In Chapter XIII we learned that the atomic weight of an element was either identical with or some multiple of its combining weight. *That factor by which we multiply the combining weight in order to get the atomic weight is the valence.* For example, the combining weight of zinc is 32.7, and its atomic weight is 65.4. The valence of zinc is two. Again, the combining weight of aluminum is 9.03, its atomic weight is 27.1, and its valence is three. In other words,

$$\text{Valence} = \frac{\text{atomic weight}}{\text{combining weight}}$$

152. Naming of compounds. The chemist writes formulas, but *does not talk formulas.* Hence it is necessary to pay close attention to the method of naming chemical compounds, for a very slight change in the name of a compound will often transform it into a compound of quite different properties. For example, mercuric chloride ($HgCl_2$) is corrosive sublimate, which is extremely poisonous; but mercur**ous** chloride ($HgCl$) is calomel, which is a common medicine.

In naming **bases**, we simply prefix the name of the metal to the word *hydroxide.* Thus we have sodium hydroxide ($NaOH$), calcium hydroxide ($Ca(OH)_2$), and aluminum hydroxide ($Al(OH)_3$).

In naming **acids**, we must distinguish between an acid consisting of two elements (a *binary acid*) and an acid consisting of three elements (a *ternary acid*). In the binary acid we have but one element beside the hydrogen; here we prefix **hydro-** to the name of the second element and add the termination

-ic. Thus we have hydrochloric acid (HCl) and hydrosulfuric acid (H_2S). The large majority of ternary acids contain oxygen as the third element. It often happens that the same three elements form more than one acid. The most familiar one is named from the characteristic element and ends in the suffix **-ic**; while the one with less oxygen has a similar name, but the ending is the suffix **-ous**. Thus we have sulfuric acid (H_2SO_4) and sulfurous acid (H_2SO_3); also nitric acid (HNO_3) and nitrous acid (HNO_2). The ternary acids are often called the oxygen acids, or *oxy-acids*.

In naming a salt, we have to consider very carefully the acid from which it has been derived. If the acid is a binary, then the salt is named after its two constituent elements with the ending **-ide**. Thus we have sodium chloride ($NaCl$), zinc chloride ($ZnCl_2$), and copper sulfide (CuS). If the acid is ternary and its name ends in **-ic**, then the name of the salt ends in **-ate**, but if the ternary acid ends in **-ous**, then the name of the salt ends in **-ite**. This will be made clear in the following examples:

NAME OF ACID	FORMULA	NAME OF SALT	FORMULA
Hydrochloric . . .	HCl	Sodium chloride . . .	$NaCl$
Sulfuric	H_2SO_4	Copper sulfate . . .	$CuSO_4$
Sulfurous	H_2SO_3	Potassium sulfite . .	K_2SO_3
Hydrosulfuric . . .	H_2S	Zinc sulfide	ZnS
Nitric	HNO_3	Potassium nitrate . .	KNO_3
Nitrous	HNO_2	Sodium nitrite . . .	$NaNO_2$

SUMMARY OF CHAPTER XIV

THE VALENCE of an atom is the number of hydrogen atoms with which it will combine or which it will replace. This may be represented by supposing that each atom has a certain number of hooks, or *bonds*, which enable it to join some other atom or atoms. This is merely a mechanical analogue.

A RADICAL is a group of elements that acts like a single element in a chemical reaction.

Some elements have *more than one valence*, the valence being different in different compounds.

IN WRITING FORMULAS of binary compounds the total number of bonds of one element must equal the total number of bonds of the other element.

IN REPLACEMENT REACTIONS the number of atoms which one element will replace of another can be predicted from the valences of the two elements. The total number of bonds of the replacing and replaced atoms must be equal.

$$\text{VALENCE} = \frac{\text{atomic weight}}{\text{combining weight}}$$

ALL BASES contain the hydroxyl (OH) radical and are called *hydroxides*.

THE NAME of a *binary acid* has the prefix *hydro-* placed before the name of the second element and the suffix *-ic* added. The derived *salt* has the suffix *-ide*.

THE NAME of a *ternary acid* is derived from its most characteristic element. The most familiar acid ends in *-ic* and its salt in *-ate*. The acid with one less atom of oxygen than the *-ic* acid has a name ending in *-ous*, and its salts end in *-ite*.

QUESTIONS

1. Mark the valences in the following formulas:

SO_3; CO; P_2O_5; $PtCl_4$; KI.

2. Correct the following formulas:

$ZnNO_3$; $CaCl_3$; $Cu(NO_3)_4$; $AgCl_2$; Al_3O_2.

3. Two grams of a tetravalent metal unite with 0.54 grams of oxygen. Find the atomic weight of the metal and write the formula for its oxide.

4. The atomic weight of a certain metal is 52. By experiment it is found that 26 grams of this metal replace 1 gram of hydrogen from hydrochloric acid. What is the valence of the metal in this displacement?

5. The formula for phosphoric acid is H_3PO_4. What is the formula for phosphorous acid?

6. Silver, zinc, aluminum, and tin have valences of 1, 2, 3, and 4 respectively; write the formulas for their chlorides, sulfates, and phosphates, assuming that the salts have the normal composition.

7. What is the difference in composition between potassium chlorate and potassium chloride? sodium nitrate and sodium nitrite? ferric chloride and ferrous chloride?

8. Complete and balance the following equations:

(*a*) $KOH + HCl \longrightarrow \text{——} + \text{——}$
(*b*) $NaOH + H_2SO_4 \longrightarrow \text{——} + \text{——}$
(*c*) $Ca(OH)_2 + H_2SO_4 \longrightarrow \text{——} + \text{——}$
(*d*) $Ba(OH)_2 + H_3PO_4 \longrightarrow \text{——} + \text{——}$
(*e*) $Al(OH)_3 + H_2SO_4 \longrightarrow \text{——} + \text{——}$

9. Give the names of all the salts formed in the preceding question.

10. Write the formulas of the following salts and indicate the valence of each element or radical: magnesium oxide, aluminum chloride, potassium nitrite, silver sulfate, ammonium chloride.

11. From the table of atomic weights and of valences, compute the combining or reacting weights of the following metals: zinc, magnesium, silver, aluminum, and potassium.

12. Examine the formulas under (*a*) and write the formulas under (*b*):

(*a*) SnS_2, H_3PO_4, Tl_2O, $CrCl_3$, H_2S, $Ca(NO_3)_2$, $AlPO_4$.

(*b*) Tin chloride, thallium nitrate, chromium oxide, calcium phosphate, aluminum sulfide.

13. Given the valence of B as two, derive the probable valences of A, C, and D from the following formulas:

A_2B_3, B_2C, B_5D_2. What would be the formula of a compound of A with C?

CHAPTER XV

SOLUTIONS

Solvents — saturated solutions — crystallization — supersaturation — importance of solutions — osmotic pressure — boiling points and freezing points of solutions — solution of gases in liquids — the nature of solutions — suspensions and emulsions — colloidal solutions — applications of colloids.

153. Solvents. We have seen in Chapter VI that water is a very good solvent for many substances. This is particularly true for the compounds known as acids, bases, and salts. There are several other liquids besides water which have considerable solvent power. Alcohol, for example, will dissolve a number of substances, such as shellac, which are not soluble in water. Some substances, like fats, waxes, and gums, are insoluble in water but soluble in certain organic compounds, such as ether, carbon tetrachloride, carbon disulfide, and gasolene. For this reason, when we wish to make a solution of a particular substance, we must try by experiment to find the solvent which is most suitable. This fact is taken advantage of in removing spots from clothing. If the spot is salt or sugar we use water to remove it. If it is a grease spot, however, we use gasolene or some similar substance. To remove paint from clothing we must use turpentine or ether, since these are about the only solvents which will dissolve the oily material used in paint.

154. Saturated solutions. There is a certain limit to the amount of material which a solvent will dissolve. This limit varies greatly with the nature of the material to be dissolved and the nature of the solvent. Thus, 100 grams of water at

20° C. will dissolve 34 grams of potassium chloride and only 7 grams of potassium chlorate. When a solution contains a large quantity of the material, it is said to be **concentrated**; when only a small quantity, it is **dilute**; when it contains all the dissolved substance that it possibly can take up at a specified temperature, it is said to be **saturated**. We call the maximum amount of solid which can be dissolved in 100 grams of solvent the **solubility of the substance.** This amount usually varies with the temperature. Solubility curves (Fig. 86) may be drawn by plotting temperatures horizontally and the number of grams dissolved in 100 grams of water vertically. In nearly all cases as the temperature is raised more material can be dissolved. For example, 100 grams of water will dissolve 13 grams of potassium nitrate (KNO_3) at 0° C., 26 grams at 15° C., 169 grams at 80° C.; on the other hand, the solubility of sodium chloride is more constant: 36 grams at 15° C. and 38 grams at 80° C. This difference in solubility is strikingly illustrated in figure 87. A few substances, such as calcium hydroxide ($Ca(OH)_2$), become less soluble as the temperature increases. When the maximum amount of a substance that can be dissolved is very small, we say that the substance is **insoluble**. Strictly speaking, however, no material is absolutely insoluble. For example, a saturated solution of powdered marble in water contains

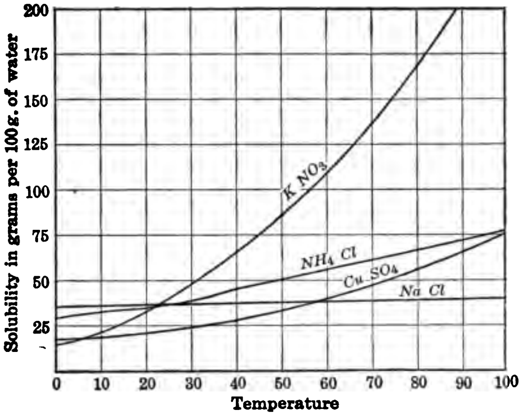


Fig. 86. Curves showing the effect of temperature on solubility.

0.00013 grams in 100 grams of water, although we say that marble is insoluble in water.

155. Crystallization. The material which is dissolved in a solution is uniformly distributed throughout the whole solution and is homogeneous to the eye. It will not separate out even on long standing. These are the essential differences between a mechanical mixture like sand and water and a true solution like sugar or salt in water. If some of the solvent is removed by evaporation from a saturated solution, the dissolved material will separate out in the form of crystals. An example of this was given in section 125, where the water evaporated leaving salt in the form of little cubes. Another way of obtaining a crystalline solid from a solution is to make a saturated solution of the substance at a high temperature and then allow it to cool. If the solubility of the material is much less at the lower temperature, a corresponding amount of solid will separate in the form of crystals. The separation of a solid from a solution in these ways is called **crystallization.**

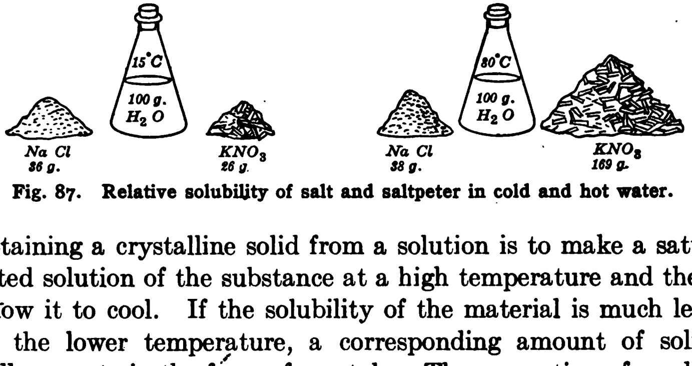


Fig. 87. Relative solubility of salt and saltpeter in cold and hot water.

Crystals can be classified into a small number of classes according to their geometrical form (see Appendix). Examples of some common minerals which occur as crystals are shown in figure 88. The crystalline forms of substances should be observed closely, for they often help to identify the substances.

Some solids take water with them when they separate from a solution. This water seems to be only loosely bound to the *rest of the molecule but to* be definite in amount. We call

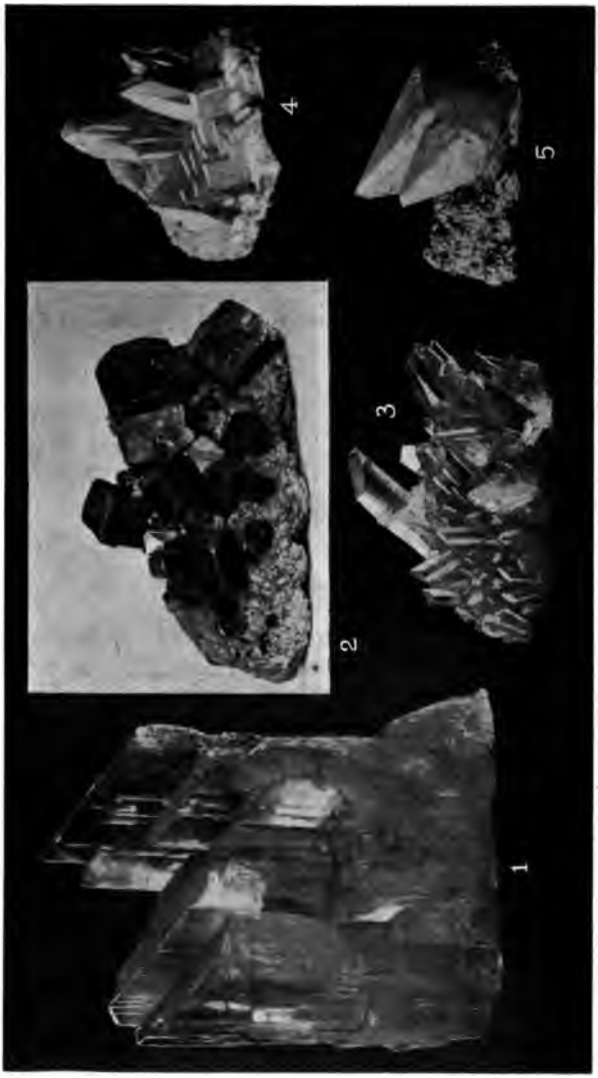


Fig. 88. Crystals of some common minerals: (1) Gypsum, (2) Galena, (3) Quartz, (4) Barite, and (5) Calcite.

it **water of crystallization** and indicate it thus in the formula: $CuSO_4 \cdot 5\,H_2O$ (copper sulfate). Such salts are often called **hydrates**, and the same salt without its water of crystallization is said to be **dehydrated**. For example, crystallized copper sulfate is blue, but dehydrated copper sulfate is white. The water of crystallization can usually be driven off simply by heating the substance; in a few cases it is so loosely held that it is lost even at room temperature. This last process is called **efflorescence**.

156. Supersaturation. Sometimes when we cool a hot, clear, saturated solution to room temperature, no crystals appear even though the solution now contains much more material than could be taken up by the solvent at this temperature. Such a solution is said to be **supersaturated**. Crystals will usually appear in it if it is allowed to stand, or if it is shaken or violently stirred. The addition of a very small crystal of the substance concerned will always bring about crystallization at once.

We may demonstrate this by preparing a hot saturated solution of sodium sulfate in a flask. We stopper the flask with cotton batting to keep out the dust and allow it to cool without moving the flask. When it is cold, we suspend in the solution a small crystal of sodium sulfate and note the rapid formation of the crystals (Fig. 89).

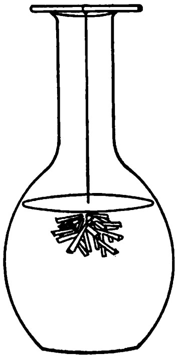


Fig. 89. Crystallization of a supersaturated solution.

157. Importance of solutions. Not only are solutions very important to the chemist, but they are vitally important to all living things. Our food must be dissolved in the course of digestion in order to pass into the blood and so be transformed into muscle and bone. Plants take in the nitrogen-containing substances and mineral matter which are in the soil only when they are in the form of solutions. These enter the roots and are conveyed as sap to the growing parts of the plants.

There are many places in our great West, formerly deserts, which have become fertile simply through irrigation. The addition of water to the land dissolved the food materials which were already in the soil and so made them available as plant food. Figure 90 shows a field before and after irrigation. *No part of the soil can act as plant food unless it is first dissolved.*

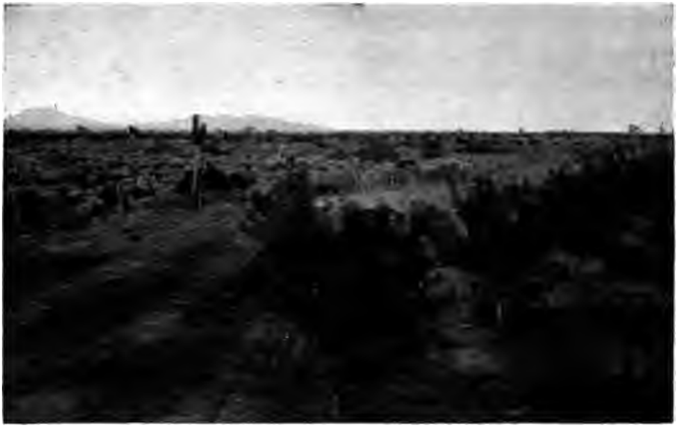


Fig. 90. Irrigation has turned this desert region (on the left) into a fertile fruit-growing region (on the right).

The question may be asked, How about "dry farming"? In some arid regions it has been found feasible to prevent the evaporation of the limited amount of moisture by deep plowing and by thorough and constant surface cultivation of the soil. After a time enough moisture may be retained to grow a crop. In certain cases the rainfall is so small that a crop can be grown only once in two years. Dry farming is simply a system of *conserving* the moisture so that the plants may have the amount of water they need to dissolve their food.

158. Osmotic pressure. The question sometimes comes up, Why does the sap rise in a tree? To explain this let us study very briefly the peculiar behavior of solutions.

By way of illustration we may perform the following experiment. We *tie parchment paper* over a small glass funnel and make the joint tight with sealing wax; then we fill the funnel with a solution of sugar and attach a long glass tube to the stem by rubber tubing. We place the funnel in a beaker of distilled water, as shown in figure 91. *The solution rises in the tube because of the passing of the water through the parchment.* After several days the solution in the tube will have reached a considerable height.

Certain thin films of vegetable and animal material tend to allow water, but not dissolved substances, to pass through them. These are called **semi-permeable membranes.** They can also be prepared artificially by precipitating certain substances into the pores of an earthenware vessel. Water passes through the membrane into the inside vessel, and a pressure is exerted which corresponds to the height of the water column. The passage of water through a membrane from a dilute to a concentrated solution is called **osmosis,** and the pressure in the inside vessel is called **osmotic pressure.** All solutions exert an osmotic pressure if they are separated by a semi-permeable membrane from pure water or a more dilute solution. *Water passes in such a direction as to cause the more concentrated solution to become more dilute.*

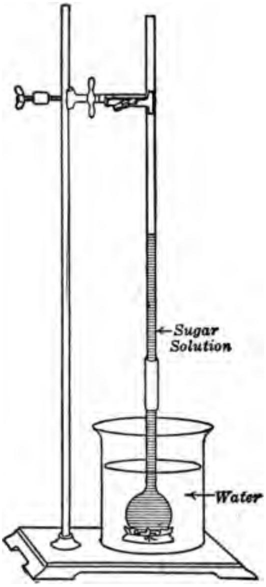


Fig. 91. **Apparatus to show osmosis.**

The water in the beaker passes through the membrane and dilutes the sugar solution; the volume being increased, it rises in the tube.

Osmosis appears to be an explanation of the action of the roots of plants. The water or dilute solution which is taken in by the cells at the root tip is passed from cell to cell farther into the root by osmosis and finally reaches the tubes or pores, through which it is carried into the stems and leaves. This process continues as long as the cell sap is a more concentrated solution than the soil water. Likewise the food we eat is changed into liquid form, passes into the blood by osmosis, and is carried throughout the body.

159. Boiling point and freezing point of solutions. Under ordinary conditions pure water freezes at 0° C. and boils at 100° C. *The addition of any soluble solid lowers the freezing point and raises the boiling point.* This lowering of the freezing point is made use of in several ways. For example, the brine which is used in refrigeration plants is a solution of calcium chloride in water. It freezes at a much lower temperature than water and therefore conducts heat away from the water which is to be frozen. Again, if we make a mixture of ice and salt, some of the melting ice forms a saturated solution of salt. A saturated solution of salt freezes at −21° C., and hence a mixture of ice, solid salt, and a solution of salt can stay together permanently only at this temperature. The result is that more ice will continue melting, thus absorbing heat until the temperature is lowered to −21° C. A mixture of this kind is called a **freezing mixture** and is used for such purposes as making ice-cream. Since salt water (the sea) freezes at a considerably lower temperature than pure water, it is only in extreme climates that harbors and bays freeze over.

160. Quantitative observations. If we dissolve in 1000 grams of water one gram-molecular weight of alcohol (C_2H_5OH), which is 46 grams, and in another liter of water a gram-molecular weight of glycerine ($C_3H_5(OH)_3$), which is 92 grams, we find that both solutions freeze at the same temperature, namely −1.86° C. We find further that both solutions boil at 100.52° C. In other words, a gram-molecule of any dissolved substance *lowers the freezing point of a given weight of water by a constant amount*, and *raises the boiling point a constant amount.* These experiments indicate that it is not the total weight of material dissolved in a given weight of water that determines the freezing and the boiling points, but rather *the number of molecules* *in solution.* This fact has furnished another method of determining the molecular weights of many solids and liquids; but we need not describe its details here.

161. Solution of gases in liquids. Thus far we have been considering the solution of solids in liquids; but we shall often have to consider the **solubility of gases in liquids.** It will help us to remember the main facts about the common gases if we divide them into three groups:

1. **Very soluble**: ammonia, hydrogen chloride, and sulfur dioxide.
2. **Fairly soluble**: hydrogen sulfide, chlorine, and carbon dioxide.
3. **Slightly soluble**: oxygen, hydrogen, nitrogen, and the inert gases.

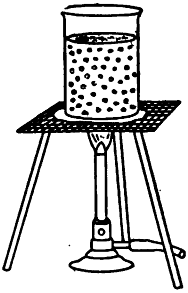


Fig. 92. Bubbles of air in water.

It has been found that an *increase of pressure always increases the quantity of gas going into solution,* and that the increase is directly proportional to the pressure. This is called the LAW OF HENRY, and was formulated in 1803. We have already noted one practical application of it in the manufacture of carbonated water (§ 65).

If we slowly heat a beaker containing cold water, small bubbles of air will be seen to collect in great numbers upon the walls (Fig. 92) and to rise through the liquid to the surface. It might seem at first that these are bubbles of steam; but they must be bubbles of air, (1) because they are formed at a temperature below the boiling point of water, and (2) because they do not condense as they come to the cooler layers of water above.

This simple experiment shows that ordinary water contains dissolved air, and that the amount of air which water can hold decreases as the temperature rises. *The solubility of gases diminishes with rising temperature.* It is the oxygen of the air *that is dissolved in water* which supports the life of fish.

162. The nature of solutions. The facts about solutions which we have been considering have led investigators to believe that solutions are in very much the same condition as gases. That is, we think of the molecules of a dissolved substance as flying around among the molecules of the solvent, much as the molecules of a gas fly about, according to the kinetic theory. If this conception of solutions is correct, when a substance dissolves in water it is really separated into individual molecules just as if it were vaporized. We can thus understand why the determining factor in the raising of the boiling point and the lowering of the freezing point is the relative number of dissolved molecules. We can further picture osmotic pressure as being due to the bombardment of the semi-permeable membrane by the molecules of the dissolved substance which cannot pass through it.

FIG. 93. JACOBUS HENDRICUS VAN'T HOFF (1852–1911).

Applied the gas laws to solutions; founder of the modern theory of solutions.

If we place a crystal of some colored substance, like copper sulfate ($CuSO_4$) or potassium permanganate ($KMnO_4$), at the bottom of a tall cylinder of water, we see the color of the material being rapidly distributed throughout the whole solution. This diffusion in a liquid is similar to the way in which one gas diffuses in the presence of another gas.

We have already seen (§ 49) a few drops of bromine (a red liquid) *poured into a tall jar of* air diffuse upward through the jar. This is *a case of diffusion of gases.*

These experiments suggest, as we have said, that the structure of solutions may be very much like that of gases. Along these lines there has been developed in the last 25 years what is practically a **kinetic theory of solutions.** If the parallel between gases and solutions is correct, then osmotic pressure should be very much like gas pressure. It has been found that the osmotic pressure of very dilute solutions follows the Laws of Boyle and Charles. This most striking evidence for the kinetic theory of solutions was worked out by the Dutch chemist, van't Hoff (Fig. 93). The theory seems to apply best to dilute solutions; with concentrated solutions it is not so satisfactory. It is probable that in both dilute and concentrated solutions there is some chemical combination between the dissolved substance and the solvent, such as there is known to be in the case of ammonia and water. If this is true, the particles which we imagine are moving around in the solution are not particles of the dissolved substances alone, but are particles of the dissolved substance combined with one or more molecules of the solvent. Some such picture as this represents our present knowledge of solutions.

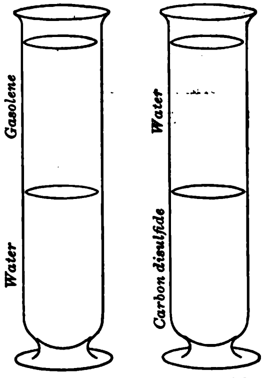


Fig. 94. Immiscible liquids.

163. Suspensions and emulsions. If we take some very finely powdered substance, such as flour, and stir it up with water, we obtain an apparently uniform mixture. On standing, the solid will slowly settle, and the mixture will thus gradually separate into solid and liquid. Such mixtures are called **suspensions.** Muddy water is a common example of a suspension.

Many liquids will dissolve in one another in all proportions; for example, alcohol and water. These substances are said to be **miscible** in all proportions. If we mix water and carbon disulfide (CS_2), we very soon notice a sharp line of separation between these two **immiscible** liquids (Fig. 94). Some liquids, such as phenol (C_6H_5OH) and water, have a limited solubility in each other, the solubility depending on the temperature.

If oil and water, two immiscible liquids, are violently shaken up together, small globules of the one may remain suspended in the other for a long time. This is a mechanical mixture like a suspension, and is called an **emulsion**. Salad dressing is such an emulsion; we make it by shaking up olive oil and vinegar together. After long standing emulsions will separate into the two liquids.

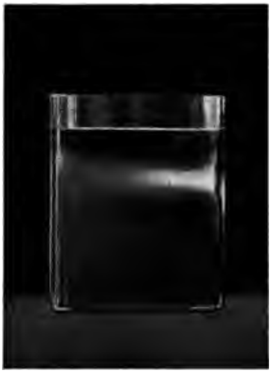


Fig. 95. A beam of light shining through a colloidal solution of starch.

The difference between solutions on the one hand and suspensions and emulsions on the other is probably due to the size of the particles. In a solution we have molecules distributed throughout the liquid which are very small and move about rapidly. In suspensions and emulsions the particles are many thousand times larger than molecules and can be seen with a microscope.

164. Colloidal solutions. Between the true solutions and the suspensions and merging into both we have what is known as colloidal solutions, or **colloids**. Colloidal solutions usually look perfectly clear to the naked eye, but when a beam of light is thrown through them they can be seen to be not entirely homogeneous.

If we put some starch into cold water we find that it is not soluble, but forms a suspension. But if we boil it in water the grains of starch swell and break, and the starch becomes finely diffused throughout the water. This clear liquid is a colloidal solution. When the liquid is poured through a filter paper, almost all the *starch goes through the paper*. On cooling, the liquid becomes a clear, stiff jelly.

If we pass a beam of light through a solution of common salt, we see no distinct path because the molecules are too small to reflect light. But if we pass a beam of light through the clear colloidal solution of starch we see the bright path (Fig. 95).

The size of the particles of the dissolved substance in a colloidal solution lies between the size of those in a true solution and those in a suspension. They are so small that they can move with some freedom, and they never settle out as do suspensions. On the other hand, they probably do not move around as freely or as rapidly as dissolved molecules because they are so much larger. Colloidal solutions exert a very small osmotic pressure and have almost the same freezing and boiling points as the pure solvents. This shows that the dissolved particles are very large.

165. Applications of colloids. The importance of the study of colloids in chemistry can be estimated when we realize that a very large part of living matter is made up of colloidal substances. The cells of plants and of animals; part of the blood; the sap of trees like rubber; much of our food, the proteids for instance — these are typical examples of colloids. They are furthermore of great importance in the industries: the process of tanning leather and of dyeing, the making of artificial silk and of glass involve a knowledge of colloids.

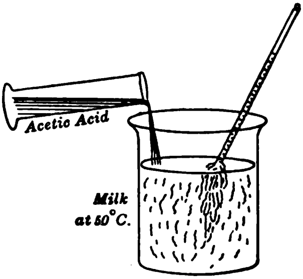


Fig. 96. Coagulation of casein in milk through the addition of acetic acid.

Glue and gelatin well illustrate some of the properties of colloids. Colloidal solutions of a number of such simple substances can be prepared. Some of these, like glue, are very stable and can be preserved for a long time; others are unstable and on being treated with small amounts of certain substances or on being heated precipitate the colloidal material. This process is often spoken of as **coagulation.** For example, the colloidal material in milk — casein — can be rapidly coagulated at 50° C. by the addition of a little acetic acid (Fig. 96). This same change takes place slowly in the preparation of junket with the aid of rennet and in making cheese.

Some colloidal solutions on cooling or on evaporation turn into jelly-like materials which are called **gels**. The most familiar example is gelatin, a 5 per cent solution of which turns into a gel at 18° C. Gels go back into colloidal solutions if we warm them or add more water. They all contain a great deal of the solvent although they are very rigid solids. For this reason a relatively small weight of a dry substance like gelatin will in solution produce a large amount of gel. All the fruit jellies which are made directly from the fruit are gels; a colloidal substance, pectin, which is present in the fruit, causes the gel to form. **Solid alcohol** is a gel formed by dissolving a colloidal substance (stearic acid) in denatured alcohol.

SUMMARY OF CHAPTER XV

WATER is the common *solvent* for acids, bases, and salts. Many substances which are insoluble in water will dissolve in alcohol, ether, carbon tetrachloride, or gasolene.

A SATURATED SOLUTION is one which contains in solution all of a given substance which it can acquire. A saturated solution on cooling sometimes becomes *supersaturated*.

SOLUBILITY is expressed as the number of grams of a substance that will dissolve in 100 grams of the solvent. This changes with the *temperature*, usually increasing rapidly with an increase of temperature.

CRYSTALLINE SOLIDS separate from solutions on evaporation, or when a saturated solution is cooled.

WATER OF CRYSTALLIZATION is the definite amount of water with which some substances rather loosely combine when they separate from a solution as crystals.

AN EFFLORESCENT substance loses its water of crystallization at room temperature.

OSMOSIS is the process by which water passes through a *semi-permeable membrane* which holds back dissolved substances.

Dissolving a substance in a solvent *lowers the freezing point* and *raises the boiling point* in proportion to the *number of molecules* present.

SOLUTIONS are believed to have a *structure much like gases.* The molecules of the dissolved substance fly about among the solvent molecules.

SUSPENSIONS AND EMULSIONS are mechanical mixtures of solids and liquids, and of liquids and liquids, respectively.

COLLOIDAL SOLUTIONS contain particles between the size of molecules and those in suspension. Colloidal solutions look clear, but a beam of light shows that they are not homogeneous.

QUESTIONS

1. Define and illustrate the meaning of these terms: *solvent, insoluble, saturated, dilute solution, supersaturated solution, colloidal solution, suspension,* and *emulsion.*

2. Compare the freezing point of Great Salt Lake and of Lake Erie.

3. What two tests could you apply to a solution to show that it was colloidal?

4. How would you determine whether a given solution is unsaturated, saturated, or supersaturated?

5. Crystals of washing soda become covered with a coating of white powder. Have they gained or lost weight? Explain.

6. What other substances besides salt could be used with the ice in an ice-cream freezer?

7. Why is a solution not considered a chemical compound?

8. Why does stirring or shaking make a solid dissolve more rapidly in a liquid?

9. How do you explain the foam on ginger ale after it is opened and poured into a glass?

10. What is the difference between the action of hydrochloric acid on zinc and the action of water on sugar?

11. The white of a raw egg is a colloidal solution. How could you coagulate it?

TOPIC FOR FURTHER STUDY

Colloids. What common household substances are colloidal gels? How can they be liquefied? What happens when milk stands for some time? Why doesn't the same thing happen to a gelatin solution? (*Findlay's* Chemistry in the Service of Man.)

CHAPTER XVI

THE THEORY OF IONS

Electrolytes and nonelectrolytes — abnormal behavior of electrolytes — ionization — electrolysis — acids and bases — neutralization — degree of ionization — ionic reactions — reactions which go to completion — rules for solubility — valence of ions — the electron.

166. Solutions as electrical conductors. Solutions of different substances in water vary greatly in their power to conduct an electric current. Some solutions will not conduct the current at all; others conduct it very readily. Let us try to understand the reason for this difference.

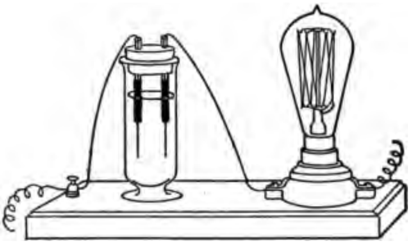


Fig. 97. Apparatus to show conductivity of solutions.

We may study the conducting power of solutions, roughly, with apparatus somewhat like that shown in figure 97. The two platinum wires are connected with the electric circuit. The lamp which is on one of the wires serves as resistance to control the current and also as an indicator of the current. When it glows brightly the solution is a good conductor.

Let us use this apparatus to test distilled water and then solutions of sugar, common salt, hydrochloric acid, sodium hydroxide, acetic acid, ammonium hydroxide, and alcohol. We find that the lamp does *not light when pure water* or a solution of sugar or alcohol is used.

But the solutions of salt, sulfuric acid, and sodium hydroxide cause the lamp to burn brightly; while the solutions of acetic acid and ammonium hydroxide give only a dull red glow to the filament.

It may have been noticed that in those solutions which conduct the electric current bubbles of gas rose from the electrodes; this indicated that a chemical change was going on. Solutions of acids, bases, and salts are called **electrolytes** because they conduct electricity; pure water and solutions like those of sugar and alcohol are called **nonelectrolytes.** *A chemical change always accompanies the passage of electricity through an electrolyte,* and in this respect these conductors differ from metallic conductors.

167. Other peculiarities of electrolytes. Solutions of acids, bases, and salts are peculiar in several other respects besides that of being electrolytes. In Chapter XV we learned that one gram-molecule of a substance like sugar when dissolved in a liter of water lowered the freezing point from 0° C. to −1.86° C., and raised the boiling point from 100° C. to 100.52° C. If one gram-molecule of sodium chloride or sulfuric acid is dissolved in a liter of water, the freezing point will be lowered and the boiling point raised; but *the effect will be almost twice as great as with sugar.* All electrolytes behave in much the same way. So we say that acids, bases, and salts give *abnormal elevations* of the boiling point and *abnormal lowerings* of the freezing point. When we examine the osmotic pressure of electrolytes we find that these same solutions give *abnormally high osmotic pressure.*

We have seen that the lowering of the freezing point, the raising of the boiling point, and the osmotic pressure depend directly on the number of molecules present in a given weight of solvent. It would seem, therefore, as if an electrolyte contained a great many more molecules of dissolved substance than did a nonelectrolyte. This can be accounted for if we assume that the *molecules of a substance like salt on dissolving* *in water break up into two or more parts* which are just as free as a molecule to move about in the solution.

168. Ionization. On the basis of these facts a Swedish chemist, named Arrhenius (Fig. 98), suggested a theory which has been called the **theory of ions.** He supposed that when salt dissolved in water it was broken up, or **dissociated**, into particles of sodium and of chlorine, and that each particle carried an electric charge, a positive charge in the case of sodium and a negative charge in the case of chlorine. This process is called **ionization,** or **electrolytic dissociation**; to the charged particles Faraday (Fig. 99) gave the name **ions**, meaning "wanderers." The following equation represents the change:

FIG. 98. SVANTE AUGUST ARRHENIUS (1859–).
Suggested the theory of ionization.

$$NaCl \longrightarrow Na^+ + Cl^-$$

NOTE. An ion is indicated by writing a + or – sign after and above the symbol.

These charged particles, or ions, must not be confused with atoms; they are atoms carrying an electric charge, but this electric charge completely modifies the nature of the particle. Particles of sodium could not be floating around in an aqueous solution, for sodium is a very active metal which would immediately react with the water. The sodium ion is, however, quite different and does not react with the water.

We can now explain by the theory of ions the abnormal behavior of electrolytes in regard to the elevation of the boiling point, the lowering of the freezing point, and the osmotic pressure. Since the molecules split up into ions, we have, for example, in a solution of common salt twice as many particles as in an equimolecular solution of sugar, which is a nonelectrolyte.

FIG. 99. MICHAEL FARADAY (1791–1867).

Began as Davy's assistant. Made important discoveries in electricity and chemistry.

169. Electrolysis. Let us now apply this theory to explain *two facts* about electrolytes: namely, that they *conduct* electricity, and are at the same time *decomposed* by the current. We shall suppose that we have some hydrochloric acid in a beaker with two electrodes dipping into the solution, as shown in figure 100. According to our theory the solution contains, besides the water (which is only very slightly ionized), hydrogen chloride (HCl) molecules, hydrogen ions (H^+), and chlorine ions (Cl^-), all flying around among the water molecules. When the electrodes are connected to some source of electricity, such as a generator (*G*) or a storage battery, one electrode becomes positively (+) charged and is called the anode, while the other electrode becomes negatively (−) charged and is called the cathode.

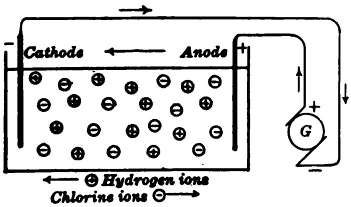


Fig. 100. Diagram illustrating the electrolysis of hydrochloric acid (HCl).

Electrical engineers often speak of electricity as "juice" because they think of it as a fluid flowing along a conductor. It is conventional to say that the electric current flows through a conductor from the positive (+) end to the negative (−). So in the case of the electrolyte, we speak of the current as *flowing through the solution from the anode to the cathode.*

According to the theory of ions, the negative electrode (cathode) attracts the positive ions (H^+) and repels the negative ions (Cl^-). This is merely the well-known law of electricity that *like charges repel and unlike charges attract.* At the same time the negatively charged ions (Cl^-) are attracted by the positive electrode (anode), and the positive ions (H^+) are repelled by it. Thus we see that when the electric circuit is closed the ions begin to migrate to their proper electrodes. In an electrolyte the ions themselves move and actually carry the electricity with them. Nonelectrolytes do not conduct electricity simply because they do not furnish the ions to carry it.

When the positive ion — in this case the hydrogen ion — reaches and touches the cathode, its positive charge is neutralized, and the result is an ordinary hydrogen atom. But we have already found that atoms of free hydrogen unite in pairs to form molecules (H_2), and so we see bubbles of the gas. At the same time the negative ions are discharged at the anode, and chlorine is set free. (At first this is largely dissolved in the hydrochloric acid.)

We thus find that the theory of ions gives us a very satisfactory account of the electrolysis of an aqueous solution, such as dilute hydrochloric acid. Sometimes the process is complicated by the fact that the atoms which are freed at the electrodes react with the water as fast as they are formed. This is the case with sodium hydroxide. The sodium atoms which are formed at the negative electrode immediately react, forming more sodium hydroxide and hydrogen. The hydroxyl ions, when the charge is removed, immediately break down into water and oxygen. Thus the gases which are produced at the two electrodes are hydrogen and oxygen, and sodium hydroxide is continually regenerated. The equations are:

$$NaOH \longrightarrow Na^+ + OH^-$$

at the negative electrode:

$$2\,Na + 2\,H_2O \longrightarrow 2\,NaOH + H_2$$

at the positive electrode:

$$4\,OH \longrightarrow 2\,H_2O + O_2$$

170. Acids and bases. We can now more clearly understand the essential characteristics of acids and bases. When an acid like hydrochloric acid dissolves in water, it dissociates into a hydrogen ion (H^+) and some other negative ion, in this case the chlorine ion. All acids dissociate, giving hydrogen ions, and we may thus define ***acids** as substances which dissolve in water and give hydrogen ions.*

All bases contain the hydroxyl group. On dissolving in water they dissociate into a positive ion, usually a metal, and the negative hydroxyl ion (OH^-). We can define ***bases** as substances which dissolve in water with the production of the hydroxyl ion.* All the characteristics of acids are really peculiarities of the hydrogen ion, and the characteristics of bases are due to the hydroxyl ion. In the case of dibasic acids, such as sulfuric acid, two hydrogen ions are produced; and in the case of bases, such as calcium hydroxide, two hydroxyl ions are produced:

$$H_2SO_4 \longrightarrow 2\,H^+ + SO_4^{--}$$

$$Ca(OH)_2 \longrightarrow Ca^{++} + 2\,OH^-$$

171. Neutralization. We have seen that when an acid and a base are brought together, water and a salt are formed. In terms of the ionic theory this means that the hydrogen ion of the acid and the hydroxyl ion of the base unite to form water:

$$H^+ + OH^- \longrightarrow H_2O$$

This reaction takes place because the molecules of water are very slightly dissociated. A molecule of water shows very little tendency to dissociate into a hydrogen ion and a hydroxyl ion. When we neutralize hydrochloric acid with sodium hydroxide, there are thus formed undissociated water molecules. The sodium ions and the chlorine ions are not affected; they still move around freely in the solution:

$$Na^+ + OH^- + H^+ + Cl^- \longrightarrow Na^+ + Cl^- + H_2O$$

The solution, however, is electrically neutral since there are an equal number of positive and negative ions. We now have exactly the same condition at hand as if we had started with salt and had dissolved it in water. As we evaporate the solution and it becomes more concentrated, a certain number of the sodium and chlorine ions join, forming undissociated sodium chloride molecules. As soon as the solution becomes saturated, these undissociated molecules begin to join together, and solid crystalline sodium chloride separates out.

172. Degree of ionization. The process of ionization is a reversible one. In concentrated solutions there are a number of undissociated molecules. As we dilute such a solution, more and more of these molecules dissociate until we find that we have only ions present:

$$NaCl \rightleftharpoons Na^+ + Cl^-$$

Thus it is only in dilute solutions that we can neglect the effect of the undissociated molecule. There are certain substances whose molecules dissociate much less readily than do common salts. Such a substance is acetic acid. Even in dilute solutions only a small fraction of the total number of molecules of this acid are dissociated into hydrogen ions and negative ions. The result is that when we compare a solution of acetic acid with one of hydrochloric acid (which has the same number of molecules in a given volume), there are many times the number of hydrogen ions in the hydrochloric acid solution more than there are in the acetic acid. That is, the concentration of hydrogen ions in the solution of acetic acid is relatively low. Acids of this sort are said to be **weak acids.** Because they have a relatively small concentration of ions, they conduct the electric current only feebly; and because the hydrogen ion concentration is low, they are only slightly acidic.

In the same way some bases, like ammonium hydroxide and copper hydroxide, are only slightly dissociated and are said to be weak bases. It must be remembered in comparing the strength of different acids and bases that we are comparing the *relative* degree of dissociation in *dilute* solutions. In order to compare the properties of the dilute solutions of two acids, we must take solutions of such strength that there will be an equal number of molecules in a given volume of each solution. In such equimolecular solutions the number of hydrogen ions will therefore vary directly with the **strength** of the acids.

Hydrochloric and nitric acids are strong acids. They are almost completely dissociated in dilute solutions. Sulfuric acid is also a strong acid, although it is not quite so strong as the two just mentioned. Acetic and sulfurous acids are weak acids; hydrogen sulfide and carbonic acids are exceedingly weak acids. Sodium, potassium, and calcium hydroxide are strong bases; ammonium hydroxide is a weak base.

173. Ionic reactions. Reactions in aqueous solutions are characterized by the fact that nearly all of them occur almost instantly. The reason for this is that these reactions take place between ions. For example, an acid neutralizes a base so rapidly that we cannot measure the speed. In general, we can think of all reactions which take place in dilute solutions of acids, bases, and salts, as being between ions. We can often write such reactions by forming equations in which the ions are shown; the neutralization reaction has already been written in this way.

The replacement of the hydrogen of an acid by a metal is really the transfer of the electricity from a hydrogen ion to a metallic atom; the metallic atom is thereby turned into a metallic ion and free hydrogen is liberated. Such a reaction can be represented thus:

$$Zn + 2\,H^{+} \longrightarrow Zn^{++} + H_2$$

The negative ion of the acid need not be shown in such an equation, because it is not involved in the reaction.

When we mix a solution of sodium chloride and potassium nitrate, nothing happens. The various ions merely move around freely in the solution. A certain number of undissociated potassium chloride and sodium nitrate molecules are produced:

$$Na^+ + Cl^- + K^+ + NO_3^- \rightleftharpoons KCl + NaNO_3$$

As both of these substances are soluble in water, they do not separate out, but dissociate again into the original ions. When we make a mixture of sodium chloride and silver nitrate ($AgNO_3$), we at once get a white precipitate. This is because the silver ions and chlorine ions combine to form undissociated silver chloride ($AgCl$) molecules, which are immediately removed from the solution since silver chloride is insoluble. In this way the reaction goes to completion: more and more sodium ions and chlorine ions unite, and more and more silver chloride is precipitated, until either the chloride ions or silver ions are exhausted:

$$Ag^+ + Cl^- \longrightarrow AgCl \downarrow$$

Fig. 101. Reaction goes to completion because a gas is evolved.

174. Reactions which go to completion. We may divide all double decomposition reactions which go to completion in aqueous solution into *three classes:*

(1) If one of the products of the action is a *gas insoluble* in water, it will escape, and the action will therefore run to an end. Such a case is the action of dilute hydrochloric acid on sodium carbonate (Fig. 101):

$$2\,HCl + Na_2CO_3 \longrightarrow 2\,NaCl + H_2O + CO_2 \uparrow$$

When we mix dilute sodium chloride and dilute sulfuric acid, we do not get the same result since hydrogen chloride is soluble in water. We merely have a mixture of the various ions, no molecules being formed or removed. When we use concentrated acid and heat the mixture, a reaction takes place because hydrogen chloride is now expelled.

(2) Ionic reactions will go to completion if an *insoluble precipitate* is formed. This case has already been discussed in connection with the precipitation of silver chloride. Another example is the formation of barium sulfate (Fig. 102):

$$Ba^{++} + 2\,Cl^- + 2\,H^+ + SO_4^{--} \longrightarrow BaSO_4\downarrow + 2\,H^+ + 2\,Cl^-$$

(3) Ionic reactions will also run to completion if one of the possible products is *only slightly dissociated.* The commonest example of this is the process of neutralization, which has already been considered.

175. Substances insoluble in water. In order to use the foregoing principles we shall need to know what substances are insoluble in water, or soluble only with difficulty. We have already (§ 161) considered the case of gases. We shall now state some rules for the solubility of solids which it will be well to remember.

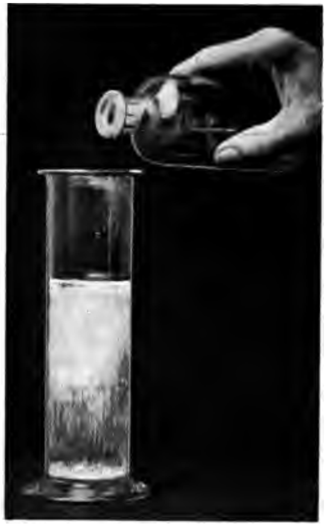


Fig. 102. Reaction goes to completion because a precipitate is formed.

General Rules for Solubility

1. All *sodium, potassium,* and *ammonium* compounds are *soluble* in water.
2. All *nitrates, chlorates,* and *acetates* are *soluble* in water.
3. All *chlorides* are *soluble,* except those of silver, mercury (mercurous), and lead (lead slightly soluble).
4. All *sulfates* are *soluble,* except those of barium, lead, and calcium (calcium slightly soluble).

5. All *carbonates* are *insoluble*, except those of sodium, potassium, and ammonium.

6. All *oxides* and *hydroxides* are *insoluble*, except those of ammonium, sodium, potassium, and barium (calcium hydroxide slightly soluble).

176. Valence of ions. Monovalent elements like sodium and chlorine form ions which have only one electric charge. However, certain elements and groups of elements form ions which have more than one charge. For example, when sodium sulfate dissociates, it forms two monovalent sodium ions and one divalent sulfate ion:

$$Na_2SO_4 \longrightarrow 2\,Na^+ + SO_4^{--}$$

VALENCE OF SOME COMMON IONS

Positive Ions			Negative Ions		
Monovalent	Divalent	Trivalent	Monovalent	Divalent	Trivalent
H^+ Na^+ K^+ Ag^+	Ca^{++} Ba^{++} Mg^{++} Cu^{++} Zn^{++} Fe^{++}	Al^{+++} Fe^{+++}	OH^- Cl^- Br^- I^- NO_3^- OCl^-	SO_4^{--} CO_3^{--} SO_3^{--} S^{--}	PO_4^{---}

It will be seen that all the *metals* form *positive* ions but that many differ in their valence. The valence of these ions, however, corresponds to the valence of the metals as we have previously learned them (§ 148). Certain nonmetals form single ions, and many of them form ions of a complex nature which contain oxygen. The valence of the nonmetallic ions likewise varies. It will help us to appreciate what is meant by valence if we recognize that the valence of a positive ion is the number of positive charges that each atom gains on going *into the ionic condition.* Similarly, the valence of a negative ion represents the number of negative charges which these atoms or groups of atoms hold. It will be seen that in order to have an electrically neutral solution a substance must dissociate in such a way that the algebraic sum of the total charges will be zero. That is, sodium sulfate could not have the formula $NaSO_4$ because it would then dissociate so that there would be twice as much negative electricity as positive. There must be two positive ions to counterbalance the doubly charged negative ion.

$$\text{Impossible} \quad NaSO_4 \longrightarrow Na^+ + SO_4^{--}$$
$$\text{Actual} \quad Na_2SO_4 \longrightarrow 2\,Na^+ + SO_4^{--}$$

177. The electron. When the ionic theory was first proposed little was known about the nature of electricity, and very little was said about the nature of the charges in the ions. It was necessary to assume, of course, that there must always be an equal number of positive and negative ions because a solution is electrically neutral; that is, it is neither positively nor negatively charged. Recent developments in physics have given us a clearer idea about the nature of electricity.

In common salt, we think that each of the sodium and chlorine atoms contains a minute nucleus of positive electricity, which comprises most of the mass of the atom. Around the nuclei there are many tiny particles of negative electricity called **electrons.** Each one of these electrons weighs about one eighteen hundredth ($\frac{1}{1800}$) as much as an atom of hydrogen. When we dissolve such a substance as salt in water, we provide an opportunity for the charged sodium and chlorine atoms to separate and move around freely. Thus, a chlorine ion (Cl^-) consists of an atom of chlorine *plus* one electron ($Cl+\epsilon$), which it has gained from the sodium atom; a sodium ion (Na^+) is an atom of sodium *minus* one electron ($Na-\epsilon$). The sodium ion is positively charged because the atom has lost one unit of negative electricity; the chlorine ion is negatively charged because *the atom* has gained this negative electricity.

When these ions combine, the resulting molecule (NaCl) is electrically neutral.

The electron is the smallest quantity of electricity which can be transferred from one atom to another, and the smallest quantity of electricity that is capable of existing alone. The positive unit of electricity is unknown in the free state, and apparently exists only when combined or associated with matter.

A "current" of electricity is regarded as a stream of electrons flowing along the conductor. It should be noted, however, that the stream or procession of electrons is flowing in the *opposite* direction from that of the electric current.

SUMMARY OF CHAPTER XVI

AQUEOUS SOLUTIONS which will conduct an electric current are called *electrolytes;* solutions which will not conduct the current are called *nonelectrolytes.* Solutions of acids, bases, and salts are electrolytes.

ALL ELECTROLYTES show an *abnormal* lowering of the freezing point, an *abnormal* raising of the boiling point, and an *abnormally* high osmotic pressure.

THE IONIC THEORY assumes that in solutions of electrolytes the molecules are dissociated into charged particles called *ions.*

ELECTROLYSIS involves the discharge of the positive and negative ions at their respective electrodes with resulting chemical change.

ACIDS are substances which produce *hydrogen ions* by electrolytic dissociation.

BASES are substances which produce *hydroxyl ions* by electrolytic dissociation.

NEUTRALIZATION merely involves the *combination* of a *hydrogen ion* and a *hydroxyl ion* to form an undissociated molecule of water.

IONIZATION is a reversible process and is *complete only in dilute* solutions. Some acids and bases are only *slightly* dissociated; they are said to be *weak.*

VALENCE of an ion is the *number* of electric charges in it.

Reactions go to completion,

(1) if one of the products is a *gas* insoluble in water;
(2) if an *insoluble precipitate* is formed;
(3) if one of the possible products is *only slightly ionized.*

QUESTIONS

1. How can you determine whether kerosene is an electrolyte?

2. When dry sodium hydroxide is treated with dry hydrogen chloride, no chemical change takes place. Explain.

3. What *five* series of *facts* indicate the truth of the theory of ions?

4. How would you define a salt in terms of the theory of ions?

5. Describe the electrolysis of hydrochloric acid in terms of the electron theory.

6. Write the ionic equation for the following reactions:

Zinc and hydrochloric acid
Potassium hydroxide and sulfuric acid
Calcium hydroxide and hydrochloric acid
Aluminum and hydrochloric acid
Sodium and water

7. When cold concentrated sulfuric acid is added to zinc, there is no change. Explain.

8. What is the distinction between a *strong* acid and a *concentrated* acid?

9. When silver nitrate ($AgNO_3$) solution is added to potassium chlorate ($KClO_3$) solution, no precipitate is formed. When silver nitrate solution is added to potassium chloride (KCl) solution, a white precipitate is formed. Explain carefully.

10. Define the following terms: *electrode*, *electrolyte*, *electrolysis*, *electrolytic dissociation*, and *electron.*

11. What are the properties of the hydrogen atom? of the hydrogen ion?

12. Which of the following substances would you expect to be insoluble in water: copper sulfate, lead nitrate, mercuric oxide, barium hydroxide, zinc nitrate, sulfur dioxide, tin oxide, aluminum sulfate, ammonium chloride, calcium carbonate?

13. Write the formulas of the soluble substances named in question 12, and indicate the ions and the valences.

14. A gram-molecular solution of sodium chloride froze at –3.42° C. Was the ionization complete?

15. When dry sodium bicarbonate and dry tartaric acid (baking powder) are mixed, there is no action. When water is added there is violent effervescence. Explain.

REVIEW QUESTIONS

1. Using the language and symbols of the ionization theory, state what happens when copper sulfate is dissolved in water.

2. Explain fully according to the ionization theory what happens when a solution of sodium sulfate is added to a solution of barium chloride.

3. What happens to the hydrogen of hydrochloric acid when this acid is neutralized by an alkali? Give the reason for your answer.

4. State accurately Avogadro's theory. Explain its use in determining molecular weights.

5. Define *element; compound; atom; molecule.*

6. How many cubic centimeters of hydrogen gas, measured under standard conditions, would be necessary to reduce 10 grams of copper oxide?

TOPIC FOR FURTHER STUDY

Sir Humphry Davy and his brilliant pupil Michael Faraday. Which man did more for the advancement of chemistry, Davy or Faraday? (*Moore's* History of Chemistry and *Thorpe's* Essays in Historical Chemistry.)

CHAPTER XVII

SULFUR AND THE SULFIDES

Occurrence of sulfur — production — experiments — properties — allotropic forms — chemical behavior.

Occurrence of hydrogen sulfide — preparation — properties — analytical uses. Carbon disulfide.

Use of sulfur in rubber — comparison with oxygen.

178. Importance and occurrence of sulfur. We shall now consider the element sulfur, which has been known since the earliest times. Large deposits of free sulfur occur in Sicily, Texas, and Louisiana. It is frequently found around the rims of craters and in the vicinity of volcanoes, as well as in non-volcanic regions.

There are large deposits of sulfur compounds, such as the sulfides of metals: **iron pyrite**, or fool's gold (FeS_2), **galenite** (PbS), and **zinc blende** (ZnS); also the sulfates, such as **gypsum** ($CaSO_4 \cdot 2\ H_2O$).

Mixed with saltpeter (KNO_3) and charcoal (C), sulfur has long been used in black gunpowder. Sulfur enters into the lime-sulfur mixtures used for spraying shrubs and trees; it furnishes the sulfur dioxide for bleaching and disinfecting. Perhaps most important of all is its use in the manufacture of sulfuric acid, a substance which plays a large and essential rôle in the preparation of other chemicals.

179. Industrial Production. In Sicily, where the sulfur deposits are on or near the surface of the ground, a very simple but wasteful method of production is employed. The sulfur mixed with considerable rock and dirt is piled up in heaps on a slanting hearth and is set on fire. *Some of the* sulfur burns, and the heat it gives out melts the rest so that it runs down the sloping floor away from the impurities. The crude sulfur is then purified by distillation, a process which is carried out by boiling the sulfur in a retort *B* (Fig. 103) and sending the vapor into a cold chamber *D*, in which it condenses. At first it collects in the form of a fine powder, which is called **flowers of sulfur.** After a time the walls of the chamber become warm, and the sulfur melts and collects on the floor *C*. It is then run into wooden molds and cast in the form of sticks. This is the ordinary **roll sulfur.**

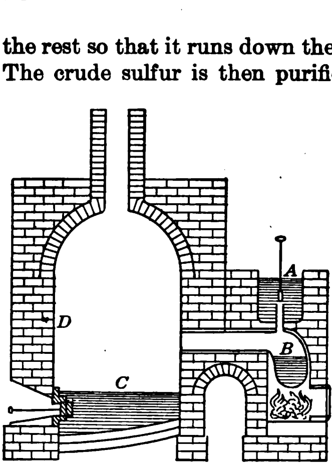


Fig. 103. Distillation of sulfur.

In America the deposits of sulfur are six hundred or more feet below the surface of the ground; and because of the surrounding clay, quicksand, and rock, it is impossible to mine it by the usual methods. An American chemist, Herman Frasch, after ten years of labor worked out a most ingenious and successful method of getting this sulfur. The process is essentially this: A hole is drilled down to the bottom of the sulfur bed. Into this hole is lowered a six-inch iron pipe which contains two smaller pipes, one within the other (Fig. 104). Water heated under pressure to a temperature well above its boiling point (170° C.) is forced down through the six-inch pipe. On coming into contact with the sulfur, the hot water melts it and turns the underground deposit into a subterranean lake of molten sulfur. Compressed hot air is now forced down through the smallest pipe and forms a froth with the molten sulfur and hot water. The pressure of the hot water and com-

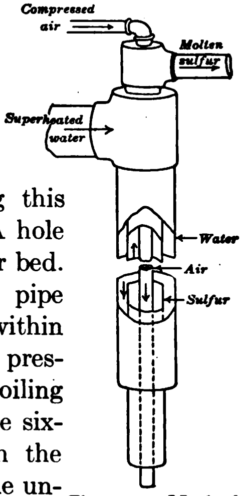


Fig. 104. Method of piping in the Frasch process.

pressed air forces this froth up through the middle pipe, whence it discharges into a large wooden bin which measures about 150 by 250 feet. In this way great quantities of sulfur can be melted and blown to the surface. It is very pure (about 99 per cent); and after it has solidified, the huge blocks are broken up, loaded directly into cars (Fig. 105), and shipped to various points for use without further purification.

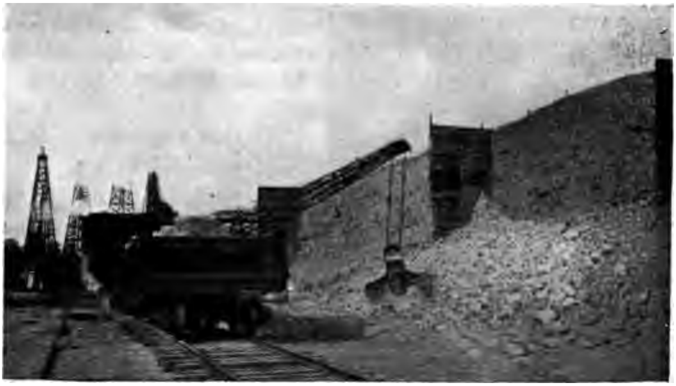


Fig. 105. Loading sulfur from the huge blocks.

The locomotive derrick takes up 2 tons at a time.

180. Experiments with sulfur. If we carefully heat some powdered sulfur in a large test tube, it easily melts and, if not overheated, gives a pale yellow liquid, which flows about the tube like oil. As we heat it more strongly the sulfur rapidly grows darker and becomes so thick and sticky that even if the tube is turned upside down it does not run out. When we heat it still more, it becomes liquid again, although it remains dark in color, and presently boils. As we let the liquid cool we note that the sulfur goes through these same changes, but in the *reverse* order.

181. Properties of sulfur. Sulfur is a pale yellow, brittle solid about twice as heavy as water. It is not soluble in water and has no marked taste or odor. When heated it melts at 114° C. to a straw-colored liquid; as the temperature rises, the liquid becomes darker and more and more viscous until at about 235° C. it is almost black and too thick to run out of the vessel. Then it grows thinner again on further heating and boils at 445° C. As a solid it is a very good insulator of heat and electricity.

182. Varieties of sulfur. If we dissolve some roll sulfur in a small quantity of carbon disulfide (CS_2) and then pour the solution into a crystallizing dish, the solvent slowly evaporates and leaves the sulfur in the shape of small crystals.

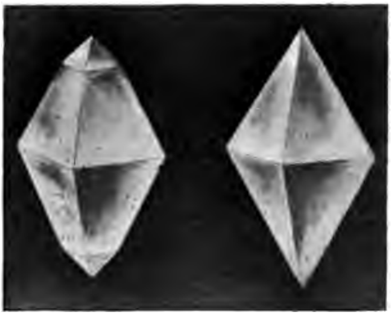


Fig. 106. Rhombic form of sulfur.

If this experiment is carried out on a larger scale and with certain precautions, more perfectly shaped crystals will be formed, like the ones shown in figure 106. These crystals generally have 8 sides (octahedral) and belong to the rhombic system; hence this variety is called **rhombic sulfur**. The free sulfur found in nature is rhombic. Roll sulfur and flowers of sulfur are largely composed of very small crystals of this sort.

Another crystalline variety can be obtained by first melting some sulfur and then allowing it to cool slowly. This can be conveniently done in a clay crucible. As the melted sulfur begins to solidify, a thin crust forms over the surface. If a hole is broken through and the liquid sulfur underneath is poured out, a loose mass of needle-like crystals (Fig. 107) is found to fill the interior of the crucible.

These crystals which grow in the liquid are of the monoclinic or **prismatic** variety. They are long, transparent, pale-yellow needles, almost rectangular in cross section and beveled at the points. Sulfur can be kept in this form indefinitely, provided the temperature is above 96° C. and below its melting point;

but when it is allowed to cool, it slowly becomes opaque because of its change into particles of rhombic sulfur.

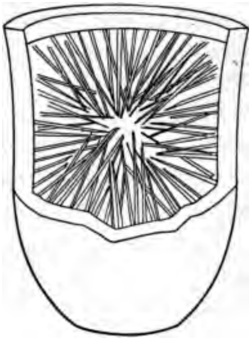


Fig. 107. Prismatic or needle-shaped crystals formed in a crucible.

We shall now heat a quantity of ordinary roll sulfur in a small flask until it is almost boiling and then pour the hot sulfur in a thin stream into a beaker of cold water, as shown in figure 108. It is convenient to place a funnel in the beaker and pour the stream of sulfur around it. Then we may easily lift out the funnel and the solidified sulfur with it. It is no longer brittle but seems almost like a gum.

The dough-like product obtained by suddenly chilling the molten sulfur in cold water is called **plastic** sulfur. Since it has no crystalline form it is also called **amorphous** sulfur. This variety is unstable and in the course of a few days changes into the rhombic form. The crystalline forms of sulfur are soluble in carbon disulfide; the amorphous forms are not.

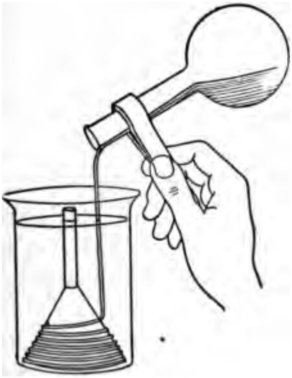


Fig. 108. Pouring melted sulfur into cold water forms plastic sulfur.

There are a number of other forms in which elementary sulfur can exist, but we shall not discuss them here.

183. Allotropic forms. The different modifications of an element, such as we have described for sulfur and such as exist also for other elements like carbon and oxygen, are called **allotropic forms.** It must not be thought, however, that the sulfur atom itself is different in these variations. The differences in form are due to the number of atoms which are combined in the sulfur molecule, and perhaps also to the way in which the atoms are grouped together. In the case of sulfur we do not yet know just how many sulfur atoms there are in the molecule of each of the different modifications; but we do know that sulfur atoms have a tendency to form large molecules, since gaseous sulfur contains a molecule which has eight atoms. In the case of the allotropy of oxygen it has been found that the difference is due solely to the fact that one form has two atoms to the molecule, while the other form (ozone) has three.

184. Chemical behavior of sulfur. All forms of sulfur behave very much alike chemically. When sulfur burns in the air it yields a pungent gas, sulfur dioxide (SO_2). Most metals when heated with sulfur unite with it directly, forming metallic sulfides.

Among the first chemical reactions which we investigated were those between iron, zinc, copper, and sulfur, forming the various sulfides. The equations for these reactions are:

$$Zn + S \longrightarrow ZnS$$

$$Fe + S \longrightarrow FeS$$

$$Cu + S \longrightarrow CuS$$

SULFIDES

185. Occurrence of hydrogen sulfide. This gas (H_2S) has a characteristic odor which is recognized whenever animal substances containing sulfur become putrid. Thus, bad eggs owe their disagreeable smell to the presence of this gas. It is also found in solution in certain sulfur springs and occurs in volcanic gases.

186. Preparation of hydrogen sulfide. When hydrogen is slowly passed over melted sulfur, the two combine to form hydrogen sulfide. Even after a few minutes a trace of the gas can be detected by means of a strip of paper moistened with lead acetate ($Pb(C_2H_3O_2)_2$) solution. The paper turns dark owing to the formation of lead sulfide (PbS), which is black.

The usual method of preparing hydrogen sulfide is by the action of dilute hydrochloric or sulfuric acid on iron sulfide (FeS):

$$FeS + 2\,HCl \longrightarrow FeCl_2 + H_2S \uparrow$$

When only a small amount of the gas is needed, the apparatus shown in figure 109 is convenient. But the Kipp generator (Fig. 25) is better when the gas is required in larger quantities. Inasmuch as the gas is somewhat poisonous, all experiments with it should be performed either under a well-ventilated **hood** or in the open air.

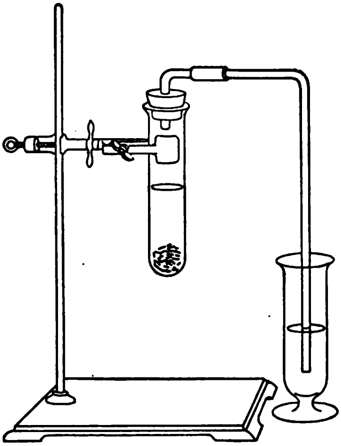


Fig. 109. Hydrogen sulfide generator.

187. Properties of hydrogen sulfide. This gas is colorless and a little heavier than air. It is fairly soluble in water, which enables us to use it in the laboratory as a solution. In pure form it acts as a poison, and even when diluted with considerable air it causes headache and nausea; but fortunately its obnoxious smell gives warning of its presence.

The gas readily burns with a bluish flame, forming water and sulfur dioxide:

$$2\,H_2S + 3\,O_2 \longrightarrow 2\,H_2O + 2\,SO_2$$

When it burns in a bottle the supply of oxygen is not sufficient to combine with both the sulfur and the hydrogen; hence the hydrogen and only a part of the sulfur burn:

$$2\,H_2S + O_2 \longrightarrow 2\,H_2O + 2\,S$$

The compound is not very stable. This can be demonstrated by holding a cold porcelain dish in the hydrogen sulfide flame

(Fig. 110). The dish shows a yellow spot due to the sulfur which is condensed on its surface. The gas in the interior of its own flame was decomposed by heat into its constituent elements.

A water solution of the gas is a very weak acid known as **hydrosulfuric acid**; it has about the same effect on litmus paper as carbonic acid (H_2CO_3). A salt results from neutralizing hydrosulfuric acid with a base. This salt is called a **sulfide**, and can be obtained by evaporating the solution.

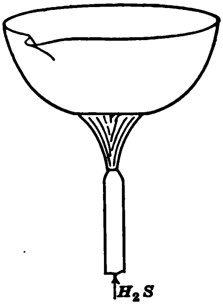


Fig. 110. Hydrogen sulfide flame deposits sulfur on a cold dish.

188. The use of hydrogen sulfide in the laboratory. Because of its action on metallic solutions, hydrogen sulfide is used as one of the reagents in analytical chemistry. The metallic sulfides which are formed have such characteristic colors that they furnish a convenient test for the presence of the metals.

Let us experiment with three solutions: (1) Dissolve a little lead acetate ($Pb(C_2H_3O_2)_2$) in some water in a test tube. (2) Dissolve a bit of white arsenic (As_2O_3) in a few drops of hydrochloric acid and then add water. (3) Dissolve a small quantity of antimony salt (tartar emetic) in water. Now pass a few bubbles of hydrogen sulfide through each solution in turn. In the first test tube we get a *black* precipitate (PbS), in the second a *yellow* precipitate (As_2S_3), and in the third a *red* precipitate (Sb_2S_3).

Thus we see that certain metallic sulfides which are insoluble in water or dilute acids can be prepared by passing hydrogen sulfide into an aqueous solution of the metallic salt.

We shall now prepare dilute solutions of copper sulfate ($CuSO_4$), iron sulfate ($FeSO_4$), and potassium sulfate (K_2SO_4), and shall then pass a few bubbles of hydrogen sulfide into each. We get a black precipitate in the copper solution and no precipitate in the other two.

If we add a few drops of ammonia water to these solutions, we get a black precipitate in the iron solution but nothing in the potassium solution.

In this experiment we note that copper sulfide (CuS) can be precipitated in an acid solution, iron sulfide (FeS) in an alkaline solution, and that potassium sulfide is precipitated in neither acid nor alkaline solutions. This furnishes a means of separating copper, iron, and potassium. The following equation will help us to understand this reaction:

$$CuSO_4 + H_2S \longrightarrow CuS \downarrow + H_2SO_4$$

In the case of iron sulfate we have a reversible reaction:

$$FeSO_4 + H_2S \rightleftharpoons FeS + H_2SO_4$$

The iron sulfide is acted upon by the dilute sulfuric acid. But by adding ammonia we neutralize this acid and thus allow the iron sulfide to form.

Some metals, like silver and lead, react directly with hydrogen sulfide to form the metallic sulfide. The tarnishing of silver in the household is probably due to the hydrogen sulfide which comes from slight leaks in gas pipes and from the burning of coal. Illuminating gas is supposed to be free from this gas, but it usually contains a trace of it.

189. Carbon disulfide (CS_2). We have already seen (§ 182) that this is a valuable solvent because it dissolves sulfur, rubber, and other substances which are not soluble in water. It is manufactured from coke and sulfur:

$$C + 2\,S \longrightarrow CS_2$$

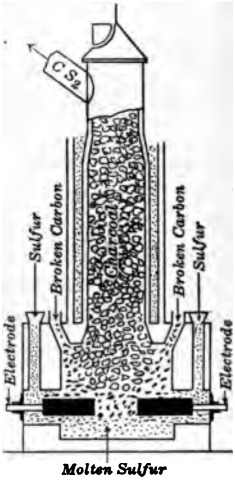


Fig. 111. Furnace for making carbon disulfide.

The reaction requires a very high temperature, which is usually obtained commercially in an electric furnace (Fig. 111). The main part is filled with coke, and the sulfur is added through the hoppers. The electric terminals are near the bottom. The heat generated vaporizes the sulfur, which unites with the hot carbon to form carbon disulfide.

Carbon disulfide is a colorless, heavy liquid which boils at 46° C. When pure the liquid is said to have a pleasant smell, but it undergoes slight decomposition, which gives it a very disagreeable odor. It is *very inflammable. Its vapors mixed with air are explosive, and consequently no flame should be near when carbon disulfide is being used.*

Besides being valuable as a solvent, it is useful in exterminating ants and other insect pests. It has also been employed to destroy the prairie dog, as well as rats and mice.

Fig. 112. Rubber tree in Sumatra. The natives gather the latex, or "juice," that has run in 24 hours.

190. Use of sulfur in making rubber. The India-rubber tree (Fig. 112), chiefly grown in the tropics, furnishes a milky juice, which is made into crude rubber by a rather primitive sort of evaporation. This material, called **caoutchouc**, is essentially a compound of hydrogen and carbon. It is soft, elastic, but unsuitable for most purposes because it very gradually oxidizes in the air and forms a brittle substance. When mixed with 10 per cent of sulfur and certain metallic compounds and then heated out of contact with the air to about 150° C., it becomes stiffer, more elastic, and much more durable. This process of **vulcanizing** produces the commercial article called rubber.

Hard rubber, also called vulcanite, is obtained when caoutchouc is mixed with from 30 to 50 per cent of sulfur and then heated to a temperature about 30 degrees higher than that applied in making the soft vulcanized rubber. Hard rubber is used in the manufacture of such articles as buttons and fountain pens; it is also a valuable insulating material for electrical machinery.

It has been found possible to prepare an **artificial rubber** which is almost identical with the natural variety. The process, however, is expensive, and the raw materials, such as potato starch or turpentine, are not cheap enough. The result is that large rubber manufacturers are laying out extensive **rubber plantations** in tropical countries in order to increase the supply of available rubber.

191. Comparison of sulfur and oxygen. Although sulfur and oxygen seem very unlike in their physical characteristics, yet in their chemical behavior they are somewhat similar. Both unite with hydrogen to form a compound containing two atoms of the latter element; that is, both are *divalent*. Oxygen unites with hydrogen much more readily and vigorously than does sulfur, but the reactions are similar in both cases:

$$2\,H_2 + O_2 \longrightarrow 2\,H_2O$$

$$H_2 + S \longrightarrow H_2S$$

Both elements combine with many metals, forming on the one hand sulfides, on the other oxides. The reactions in the case of copper will serve as an illustration:

$$2\,Cu + O_2 \longrightarrow 2\,CuO$$

$$Cu + S \longrightarrow CuS$$

The sulfides and oxides resemble each other somewhat in regard to their physical properties, such as solubility in water, etc. We shall find additional cases later on in which elements resemble each other much as do sulfur and oxygen.

SUMMARY OF CHAPTER XVII

SULFUR is found in a free state; also in sulfides and sulfates.

In Sicily it is melted away from rocky material.

In Louisiana it is melted underground by superheated water and forced to the surface.

COMMERCIALLY, sulfur is sold as flowers of sulfur and as roll or lump sulfur.

ALLOTROPIC FORMS of sulfur include the rhombic, the prismatic, and the amorphous.

The *rhombic form* is the stable form; it melts at 114° C. and boils at 445° C. It is about twice as heavy as water, insoluble in water, soluble in carbon disulfide.

SULFUR BURNS in air, forming sulfur dioxide. It combines directly with a number of elements, forming sulfides.

SULFUR IS USED in the manufacture of gunpowder, lime-sulfur spray, carbon disulfide, sulfur dioxide, sulfuric acid, and in vulcanizing rubber.

HYDROGEN SULFIDE is formed in nature by the decay of organic matter containing sulfur; it also occurs in volcanic gases and in the water of sulfur springs.

In the *laboratory, hydrogen sulfide is prepared* by the action of dilute hydrochloric or sulfuric acid on iron sulfide.

PROPERTIES OF HYDROGEN SULFIDE: a colorless gas with a characteristic unpleasant odor, fairly soluble in water, heavier than air. It burns in an abundance of air to form water and sulfur dioxide, but in a limited supply of air it forms water and sulfur.

The *water solution* is called hydrosulfuric acid; it is a weak acid and forms sulfides with most metallic solutions. Used in chemical analysis to separate metals.

QUESTIONS AND PROBLEMS

1. Describe how you would proceed to prove a yellow powder to be sulfur.

2. What properties have the allotropic forms of sulfur in common?

3. Write the names and formulas of four metallic sulfides and of the corresponding oxides.

4. Given that 22.4 liters of air weigh about 29 grams. From the formula of hydrogen sulfide compute its molecular weight and compare its density with that of air.

5. If two liters of hydrogen sulfide are burned with an abundance of air, how many liters of sulfur dioxide will be formed? What law is applied here?

6. Write the equations for the following reactions:

(*a*) lead nitrate ($Pb(NO_3)_2$) and hydrogen sulfide;
(*b*) silver nitrate ($AgNO_3$) and hydrogen sulfide;
(*c*) zinc chloride ($ZnCl_2$) and sodium sulfide;
(*d*) copper chloride ($CuCl_2$) and hydrogen sulfide.

7. Would you expect hydrosulfuric acid to be a good conductor of electricity?

8. Write the equations for making silver sulfide in three different ways.

9. How many liters of hydrogen sulfide (standard conditions) can be prepared from 500 cc. of hydrochloric acid with an excess of iron sulfide? Assume the hydrochloric acid contains 40% HCl by weight and has a density of 1.2 grams per cubic centimeter.

10. How many grams of iron sulfide are needed to give with dilute sulfuric acid 5 liters of hydrogen sulfide at 15° C. and 60 cm.?

11. Carbon disulfide is burned in air so that 1 liter of carbon dioxide is formed. How many liters of sulfur dioxide are produced?

12. When hydrogen sulfide is passed into zinc sulfate solution, the reaction is reversible. How would you make it complete?

13. What is meant by saying that hydrosulfuric acid is weak?

14. Write as an ionic equation the reaction of copper sulfate and hydrogen sulfide.

TOPIC FOR FURTHER STUDY

Rubber. When was rubber first used? Why has it become so important during the last twenty years? How can rubber be made synthetically? What is the difference between plantation and native rubber? (*Slosson's* Creative Chemistry, *Tilden's* Chemical Discovery and Invention, *B. F. Goodrich Co.'s* Wonder Book of Rubber.)

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CHAPTER XVIII

OXIDES OF SULFUR AND THEIR ACIDS

Sulfur dioxide — preparation and properties. Sulfurous acid — its uses — sulfites and bisulfites.

Sulfur trioxide — preparation and properties. Manufacture of sulfuric acid — properties of concentrated and dilute — sulfates — test for SO_4 ion.

Acid and basic anhydrides.

SULFUR DIOXIDE AND SULFUROUS ACID

192. Preparation of sulfur dioxide. We have already seen that sulfur burns in the air and forms an oxide known as sulfur dioxide (SO_2). This gas has a choking effect familiarly known as " the smell of burning sulfur." The equation is as follows:

$$S + O_2 \longrightarrow SO_2$$

One method of preparing it commercially consists in heating strongly, or **roasting** in air, a metallic sulfide such as pyrite (FeS_2) or zinc blende (ZnS), which gives the oxide of the metal as well as sulfur dioxide:

$$2\ ZnS + 3\ O_2 \longrightarrow 2\ ZnO + 2\ SO_2$$

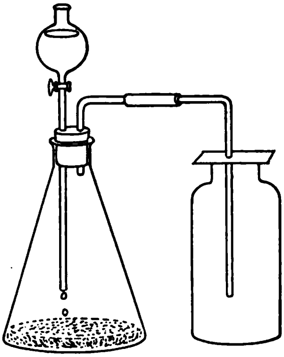

Fig. 113. Preparation of sulfur dioxide.

To prepare sulfur dioxide free from nitrogen and excess of air, we may slowly drop hydrochloric acid on crystals of sodium hydrogen sulfite (Fig. 113):

$$NaHSO_3 + HCl \longrightarrow NaCl + H_2SO_3$$
$$H_2SO_3 \longrightarrow H_2O + SO_2\uparrow$$

This reaction is simply a case of double decomposition, in which one product, the sulfurous acid (H_2SO_3), is unstable and breaks up into water and sulfur dioxide, as shown in the second equation. Another laboratory method consists in heating together concentrated sulfuric acid and copper. The products of this reaction are copper sulfate, water, and sulfur dioxide. The reaction is complicated, but the following equation represents the total change involved:

$$Cu + 2\ H_2SO_4 \longrightarrow CuSO_4 + 2\ H_2O + SO_2\uparrow$$

193. Properties of sulfur dioxide. This gas is colorless but has a characteristic sharp taste and odor. It is more than twice as heavy as air (mol. wt. $SO_2 = 64$; 22.4 liters of air weigh 29 g.), and is one of the most easily liquefied gases known. Under ordinary pressure the liquefied gas boils at −8° C. At room temperatures the liquid may be kept in stout glass bottles or metal cylinders (Fig. 114) because the pressure is only three or four atmospheres. The gas is very soluble in water, does not burn, and will not support combustion.

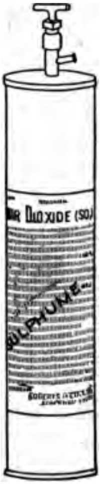

Fig. 114. Metallic container for sulfur dioxide.

194. Sulfurous acid. Sulfur dioxide not only dissolves in water, but also combines with water to form an acid known as sulfurous acid (H_2SO_3). When the water solution is heated, the acid breaks up into water and sulfur dioxide. Thus the reaction is reversible:

$$H_2O + SO_2 \rightleftharpoons H_2SO_3$$

This compound, sulfurous acid, is so unstable that it is impossible to separate it from the water in which it is dissolved.

In fact, the main reason why we believe that it exists is, that the salts of the acid can be prepared. Thus the acid solution, when neutralized by sodium hydroxide, gives, on evaporation, a substance which corresponds to the formula Na_2SO_3. This would indicate the following equation:

$$\underset{\text{sodium hydroxide}}{2\,NaOH} + \underset{\text{sulfurous acid}}{H_2SO_3} \longrightarrow \underset{\text{sodium sulfite}}{Na_2SO_3} + \underset{\text{water}}{2\,H_2O}$$

Sulfurous acid does not keep; it slowly absorbs oxygen from the air and changes into sulfuric acid. This change is expressed by the equation:

$$\underset{\text{sulfurous acid}}{2\,H_2SO_3} + \underset{\text{oxygen}}{O_2} \longrightarrow \underset{\text{sulfuric acid}}{2\,H_2SO_4}$$

On account of the readiness with which it combines with the oxygen from other compounds, sulfurous acid is a powerful **reducing agent.**

FOR EXAMPLE, potassium permanganate ($KMnO_4$) is a substance very rich in oxygen. We dissolve a crystal in water, getting a deep violet solution. We now pour this colored liquid into some sulfurous acid solution. The result is that the color is *instantly* removed because the sulfurous acid has taken some of the oxygen from the permanganate, leaving colorless compounds in solution.

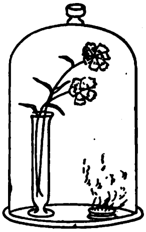

Fig. 115. Bleaching flowers with sulfur dioxide.

195. Uses of sulfur dioxide. The moist gas (that is, sulfurous acid) is used to bleach straw, silk, and wool — materials which cannot be bleached with chlorine because they become hard and brittle. The bleaching effect disappears after a time, however, and hence materials bleached by sulfur "yellow with age."

This property can be shown by placing a number of moist colored flowers near burning sulfur and then covering the whole with a glass bell jar (Fig. 115). After a short time the flowers become white.

Such foods as dried fruits and canned corn and cherries are sometimes bleached with sulfurous acid. The acid also has antiseptic properties and will prevent the fermentation of sugar, sweet cider, and preserves of various kinds. Its use as a food preservative is, however, questionable. That it is decidedly injurious to plant life is evident from the blighted vegetation in the vicinity of smelters and chemical works where this gas is allowed to escape.

By far the most important use of sulfur dioxide is in the **manufacture of sulfuric acid.**

196. Sulfites and bisulfites. When sulfurous acid is neutralized by a base, the salt produced is called a **sulfite.** If an excess of sulfur dioxide is passed into the solutions of the bases, the acid sulfite, or **bisulfite** ($NaHSO_3$), is formed. Thus:

$$NaOH + H_2SO_3 \longrightarrow NaHSO_3 + H_2O$$

In the acid sulfites, or bisulfites, there is one hydrogen atom which has not been replaced, while in the sulfite all the hydrogen atoms have been replaced.

Acids like carbonic acid (H_2CO_3), hydrosulfuric acid (H_2S), sulfurous acid (H_2SO_3), and sulfuric acid (H_2SO_4) which have *two* replaceable hydrogen atoms in each molecule are called **dibasic acids.** Hydrochloric acid and nitric acid (HNO_3) each have but one replaceable hydrogen atom per molecule and so are **monobasic acids.** Phosphoric acid (H_3PO_4) is a **tribasic acid.** The acid salt may be made by treating the acid with only half enough base to neutralize it, or by adding an excess of acid to the normal salt.

197. Use of bisulfite in making paper. When calcium hydroxide, or slaked lime ($Ca(OH)_2$), is treated with an excess of sulfurous acid, the product is calcium bisulfite ($Ca(HSO_3)_2$). This reaction is as follows:

$$Ca(OH)_2 + 2\,H_2SO_3 \longrightarrow Ca(HSO_3)_2 + 2\,H_2O$$

In making the cheaper varieties of paper, wood is cut into chips and " cooked " with a solution of calcium bisulfite. This dissolves out the objectionable constituent (lignin) of the wood, leaving the pure cellulose, which is the material desired for making paper.

SULFUR TRIOXIDE AND SULFURIC ACID

198. Preparation of sulfur trioxide. It is possible to make sulfur dioxide, when heated, combine with oxygen to a slight extent to form sulfur trioxide (SO_3). But this reaction is exceedingly slow. The rapid combination of sulfur dioxide and oxygen can be effected by the same catalyst that was used for the union of oxygen and hydrogen (§ 36), namely, finely divided platinum. The reaction, which is reversible, is as follows:

$$2\,SO_2 + O_2 \rightleftharpoons 2\,SO_3$$

At about 400° C. nearly all of the two gases unites, but above that temperature the reverse action sets in.

To illustrate this reaction one form of apparatus is shown in figure 116. We first place some platinized asbestos * in a hard-glass tube. We burn the sulfur at *S* and draw the mixture of sulfur dioxide and air through the plug *Pt* of the platinized asbestos by means of an aspirating arrangement. The plug is gently warmed. The resulting trioxide may be condensed by placing the large test tube in a freezing mixture.

199. Properties of sulfur trioxide. Sulfur trioxide is a colorless liquid, which solidifies at about 15° C. and boils at about 46° C. It exists in two allotropic forms; one is the liquid just mentioned, the other is a white crystalline solid which sublimes without melting. Sulfur trioxide combines readily with water, forming sulfuric acid. If the trioxide is thrown into water it dissolves with the evolution of much heat:

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* Clean asbestos is dipped into a rather concentrated solution of platinic chloride and then ignited over the Bunsen flame, leaving finely divided platinum throughout the asbestos.

$$SO_3 + H_2O \longrightarrow H_2SO_4$$

200. Manufacture of sulfuric acid. Enormous quantities of this acid are manufactured all over the world for use in a great variety of industries. At the present time there are two methods of manufacture: the **contact** process and the **chamber** process. In both processes the first step is the same, namely, burning sulfur or roasting a metallic sulfide to get sulfur dioxide. The chief difficulty comes in the next step; that is, in making sulfur dioxide into sulfur trioxide. This is overcome by using a **catalyst**, and here is where the principal difference between the two processes lies. In the contact process the catalyst is usually iron oxide which is kept at a definite temperature. In the chamber process the chemical changes are very complicated; the sulfur dioxide is changed to sulfuric acid by the use of steam, oxides of nitrogen, and air. The apparatus is so arranged that the oxides of nitrogen cannot escape and are used over and over again.

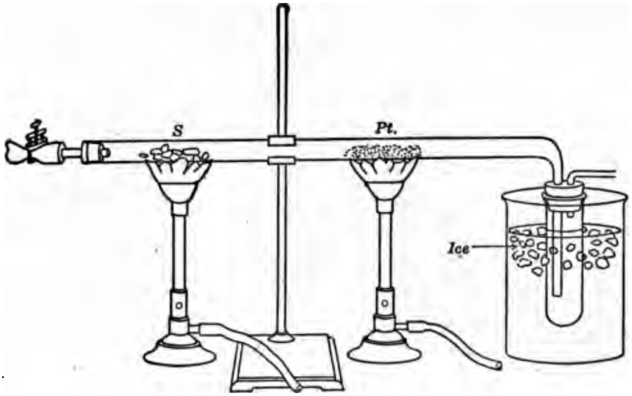


Fig. 116. Making sulfur trioxide by the contact process.

In the **contact** process (Fig. 117) the catalytic agent is ferric oxide or, as in our experiment, finely divided platinum. When prepared commercially the mixture of sulfur dioxide and air is carefully freed from dust and other impurities; for unless these are removed from the gases the platinum soon loses its catalytic power. The temperature must also be carefully regulated and kept at 400° C.; if it falls below that point the reaction is too slow, and if it rises above it the reverse reaction sets in. Finally, the sulfur trioxide is absorbed in concentrated sulfuric acid instead of in water because it has a great tendency to pass through the latter in the form of a mist, or fog, which cannot be caught. The resulting acid is called **fuming sulfuric acid**; this is essentially a solution of sulfur trioxide in concentrated sulfuric acid. On dilution with water the sulfur trioxide combines with the water and produces sulfuric acid.

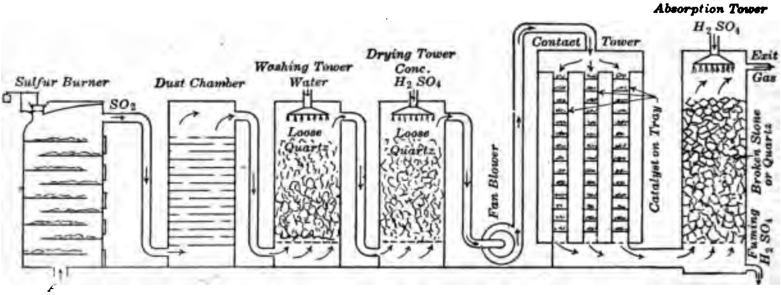


Fig. 117. Diagram of the contact process for making sulfuric acid.

In the **chamber process** (Fig. 118) the oxides of nitrogen are used as the catalytic agent. The sulfur dioxide is oxidized to sulfur trioxide by the aid of nitrogen dioxide (NO_2), a brown gas. The latter substance (NO_2) is reduced to nitric oxide (NO), but this in turn takes oxygen from the air to form the higher oxide of nitrogen again. Thus the nitric oxide, by being alternately oxidized by the air and reduced by the sulfur dioxide, acts as a carrier of oxygen. The reaction is carried out in large lead chambers. To aid in this process, as well as to furnish the necessary water to convert sulfur trioxide into sulfuric acid, steam is blown into the lead chambers.

In practice the gases from the sulfur or pyrite burners pass through a tower (Glover), which serves to cool the gases and to charge them with oxides of nitrogen. From the last of the series of chambers the gases pass through another tower (Gay-Lussac), in which the oxides of nitrogen are absorbed in concentrated sulfuric acid. This acid is then pumped to the top of the first tower, where it is diluted and gives up the oxides of nitrogen.

The acid which collects in the chambers is only about 60 per cent pure hydrogen sulfate. The chamber process is the older method and is still used extensively for making the less concentrated grades of sulfuric acid.

201. Properties of concentrated sulfuric acid. Pure sulfuric acid is a colorless, oily liquid about twice as heavy as water. Commercially it is known as **oil of vitriol** because it was formerly made by distilling green vitriol ($FeSO_4 \cdot 7\,H_2O$). It boils at a high temperature (338° C.) and is an exceedingly corrosive substance. If spilled on the skin it produces bad burns. It mixes with water in all proportions, evolving a large amount of heat. Since the concentrated acid has a great affinity for water it is used for drying many gases.

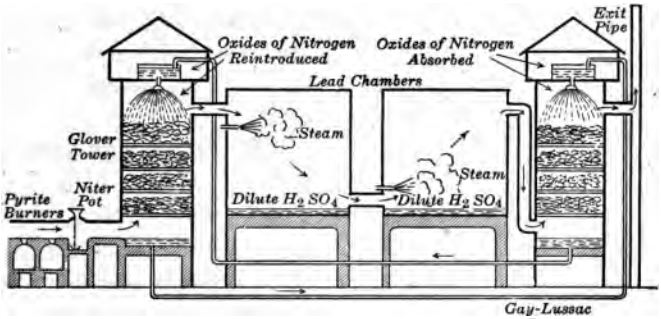


Fig. 118. Diagram of the chamber process for making sulfuric acid.

Closely connected with this avidity for water is the **dehydrating action** of the acid. It will remove hydrogen and oxygen in the form of water from many substances which contain those elements.

To show the action of sulfuric acid on paper, which is largely cellulose ($C_6H_{10}O_5$), we write with a glass rod and some dilute sulfuric acid upon white paper. We dry the paper carefully by holding it at some distance above the Bunsen flame. Where there is writing the paper turns black and charred (Fig. 119) because the dilute acid becomes concentrated through the evaporation of the water.

Hot concentrated sulfuric acid is an **oxidizing agent.** It is reduced to sulfur dioxide and water by many substances. For example, if carbon is boiled in it the carbon is oxidized:

$$2\,H_2SO_4 + C \longrightarrow 2\,SO_2 + 2\,H_2O + CO_2$$

If metals, such as silver, copper, and mercury, are used, they are converted into sulfates; and sulfur dioxide is liberated.

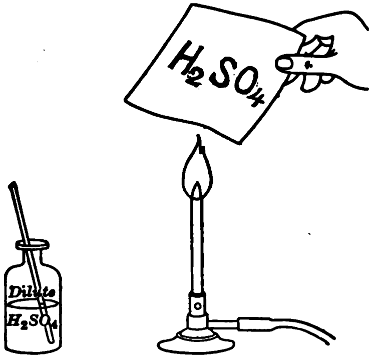


Fig. 119. Charring paper with sulfuric acid.

202. Action with salts. On account of its high boiling point, concentrated sulfuric acid is used in **preparing the more volatile acids,** such as hydrochloric and nitric acids. For example, to make hydrochloric acid we use the cheapest **chloride,** common salt:

$$NaCl + H_2SO_4 \longrightarrow NaHSO_4 + HCl\uparrow$$

The hydrogen chloride is a gas at room temperatures. It will be noted that in the above equation *sodium hydrogen sulfate* ($NaHSO_4$) is one of the products; but if we take twice as much salt and heat the salt and acid to a higher temperature, we get twice as much hydrochloric acid. This is done on a commercial scale; the equation was given in section 119.

To make nitric acid we use the cheapest of the nitrates, sodium nitrate ($NaNO_3$):

$$NaNO_3 + H_2SO_4 \longrightarrow NaHSO_4 + HNO_3\uparrow$$

The nitric acid is volatile at 86° C. If we double the quantity of sodium nitrate and heat it to a higher temperature, the nitric acid decomposes; so the actual quantity of nitric acid produced is not doubled.

203. Dilute sulfuric acid. Great care must be taken in diluting sulfuric acid because a large amount of heat is generated. *We pour the concentrated acid in a small stream into the water*, not the water into the acid. When diluted with considerable water, sulfuric acid is a **strong** acid; that is, it is largely dissociated into ions:

$$H_2SO_4 \longrightarrow 2\,H^+ + SO_4^{--}$$

It reacts with such metals as zinc, iron, and aluminum, forming free hydrogen and the sulfates of the metal. It can be neutralized with bases, forming salts. Dilute sulfuric acid has no avidity for water, is not an oxidizing agent, and obviously cannot be used for such purposes as preparing hydrogen chloride. In all these respects it differs from the concentrated acid; this distinction should be carefully noted.

204. Sulfates. The salts of sulfuric acid which contain no hydrogen are called sulfates; the salts which still have one atom of hydrogen are called bisulfates or acid sulfates. The sulfates of many metals are very important and are in common use. Thus, **plaster of Paris** is partly hydrated calcium sulfate ($2\,CaSO_4 \cdot H_2O$); **Epsom salt** is hydrated magnesium sulfate ($MgSO_4 \cdot 7\,H_2O$); the **bluestone** used in batteries is hydrated copper sulfate ($CuSO_4 \cdot 5\,H_2O$). They are for the most part crystalline solids which are soluble in water. The *sulfates of barium, strontium, calcium, and lead are insoluble.*

The **test for a sulfate**, that is, for the SO_4 ion, is the addition of a soluble barium salt (such as the nitrate) to the solution in question. If a white precipitate is formed which is insoluble in both hydrochloric and nitric acid, a sulfate is present:

$$Ba(NO_3)_2 + Na_2SO_4 \longrightarrow BaSO_4 \downarrow + 2\,NaNO_3$$

$$Ba^{++} + SO_4^{--} \longrightarrow BaSO_4 \downarrow$$

205. Uses of sulfuric acid. Concentrated sulfuric acid is employed as a drying agent both in the laboratory and in the industries. In enormous quantities it enters into the manufacture of dyes and into the production of a number of organic substances which serve as explosives. Because of its high boiling point it is used in the laboratory for the preparation of other acids from their salts. The dilute acid is used in storage batteries and in electroplating; also in cleaning the surfaces of many metals. Large amounts are consumed in the fertilizer industries. On account of its varied and extensive uses, *sulfuric acid may be considered as one of the foundation stones of modern civilization.* (See Industrial Chart, p. 205.)

206. Acid anhydrides. The two oxides of sulfur (SO_2 and SO_3) react with water to produce sulfurous and sulfuric acid respectively. An oxide which combines with water to form an acid is often called an **acid anhydride.** Another example is carbon dioxide, which reacts with water to form carbonic acid (H_2CO_3). Carbonic acid, like sulfurous acid, is unstable and on heating goes back into the anhydride. The reaction is therefore reversible:

$$H_2O + CO_2 \rightleftharpoons H_2CO_3$$

Another acid anhydride is the white oxide obtained by burning phosphorus in air. This combines with water to form phosphoric acid, which like sulfuric acid is stable and does not easily revert to the anhydride:

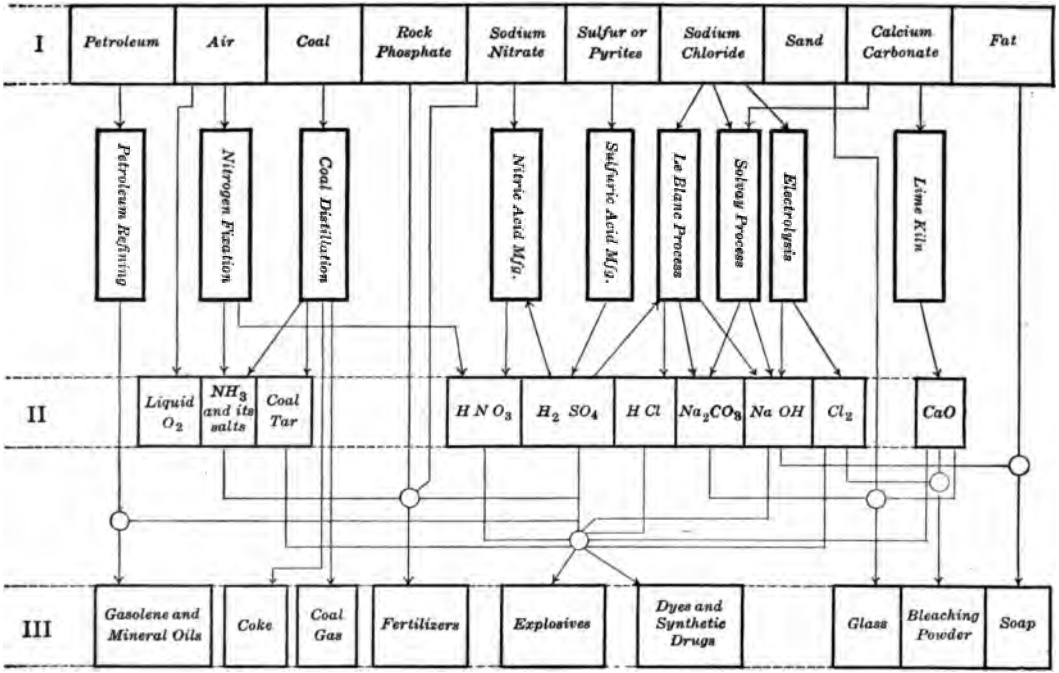
$$P_2O_5 + 3\,H_2O \longrightarrow 2\,H_3PO_4$$

The oxides of such elements as are not metals (and are therefore sometimes called **nonmetals**) are acid anhydrides. The oxides of the metals, on the other hand, unite with water to form bases. For example, calcium oxide reacts with water to form calcium hydroxide:

$$CaO + H_2O \longrightarrow Ca(OH)_2$$

INDUSTRIAL CHART

SOME OF THE MORE IMPORTANT CHEMICAL PROCESSES, THEIR RAW MATERIALS AND PRODUCTS



Row I **Raw materials** **Row II** **Chemical products** **Row III** **Important familiar materials derived from these raw materials and chemicals**

This difference in the behavior of the oxides of the nonmetals and metals is often indicated by calling the former **acidic oxides** and the latter **basic oxides.**

SUMMARY OF CHAPTER XVIII

SULFUR DIOXIDE IS PREPARED by —

(1) burning sulfur or by roasting sulfides;
(2) the action of hydrochloric acid on bisulfites;
(3) the action of hot concentrated sulfuric acid on copper.

SULFUR DIOXIDE is a colorless, choking gas which is more than twice as heavy as air. It is very soluble in water. The water solution contains sulfurous acid.

SULFUROUS ACID is unstable. It is a reducing agent. It has bleaching and antiseptic properties. It forms two classes of salts, *sulfites* and *bisulfites.*

An *acid* which has *two* replaceable hydrogen atoms is called *dibasic.*

SULFUR TRIOXIDE is formed by the union of sulfur dioxide and oxygen with the aid of a catalyst. It unites with water to form sulfuric acid.

SULFURIC ACID IS MANUFACTURED by (1) the *contact* process, in which the sulfur dioxide is oxidized with the help of a catalyst, and (2) the *chamber* process, in which the oxidation is brought about by the use of the oxides of nitrogen.

CONCENTRATED SULFURIC ACID has a strong attraction for water. When hot it is an oxidizing agent. It will drive out other acids from their salts because of its high boiling point.

DILUTE SULFURIC ACID reacts with many metals, forming hydrogen. It forms two classes of salts — sulfates and bisulfates. All sulfates are soluble except those of barium, strontium, calcium, and lead.

SULFURIC ACID IS USED in nearly all industries.

THE OXIDES OF THE NONMETALS, such as SO_2, SO_3, CO_2, P_2O_5, react with water and form *acids.* They are called *acid anhydrides*, or *acidic oxides.*

THE OXIDES OF THE METALS, like CaO, react with water to form *bases;* they are called *basic oxides.*

QUESTIONS AND PROBLEMS

1. How many grams of sulfur dioxide can be made by roasting 50 grams of iron pyrite (FeS_2)?

2. How much sulfur will be required to prepare a ton (2000 lbs.) of sulfuric acid containing 2% of water?

3. What weight of copper sulfate crystals ($CuSO_4 \cdot 5\,H_2O$) can be made from 100 grams of pure copper?

4. Why does the burning of sulfur in the air not yield *pure* sulfur dioxide?

5. What is an acid anhydride? Give the names and formulas of two anhydrides containing sulfur.

6. Name and give the formulas for the raw materials used in making sulfuric acid.

7. Which is the more stable acid, sulfurous or sulfuric acid? Give your reasons.

8. Is sulfuric acid a *stronger* acid than hydrochloric? Explain.

9. Show how the two oxides of sulfur illustrate the Law of Multiple Proportions.

10. Give two reasons why boiling sulfuric acid causes such serious burns if spilled on the skin.

11. How would you test for a *sulfide*, a *sulfite*, and a *sulfate?*

12. How could you determine whether the sulfuric acid in a bottle were concentrated or dilute?

13. What is the easiest way to bleach a straw hat?

14. Commercial sulfuric acid is generally not colorless. How do you account for the color?

15. What would happen if water were poured *into sulfuric acid?* (Don't try it!)

TOPIC FOR FURTHER STUDY

Catalysis in industry. What would appear to be the advantage of the contact process for producing sulfuric acid over the chamber process? Why has it not entirely superseded the chamber process? What other manufacturing operations use catalysts? What are some of the substances used as catalysts? (*Duncan's* Chemistry of Commerce.)

CHAPTER XIX

AMMONIA AND AMMONIUM COMPOUNDS

Household ammonia — composition and formula — preparation — properties — refrigeration — manufacture of ammonia from coal and from elements — chemical behavior — ammonium hydroxide and ammonium salts — commercial uses.

207. Household ammonia. The cleansing agent which is commonly used in the household is labeled **ammonia** or, more accurately, **ammonia water.** The name "ammonia" properly belongs to the gas which causes the familiar, peculiarly pungent smell of the cleanser. This gas is extremely soluble in water and is therefore usually sold in water solution. It owes its cleansing qualities to the fact that it is a base. Since both ammonia gas and water are volatile, it was formerly called the "volatile alkali."

208. Composition of ammonia. When we heat ammonia water, we get a gas which can be shown to be composed of nitrogen and hydrogen. To demonstrate the fact that ammonia contains nitrogen, we lead the dried gas through a tube containing hot copper oxide. We find that the copper oxide is reduced to metallic copper, water is formed, and a gas comes from the delivery tube which proves to be **nitrogen.** The presence of hydrogen in ammonia might be inferred from the formation of water, a compound of hydrogen and oxygen. But we can definitely prove that it is a constituent of ammonia by passing the gas through a tube containing heated magnesium. In this case the gas set free is **hydrogen.** The product left in the tube is magnesium nitride, which when put in water gives us ammonia again.

To determine the formula for ammonia we have only to perform the experiment with copper oxide in a quantitative way. The results of such experiments show that ammonia is 82.3 per cent nitrogen and 17.7 per cent hydrogen. Dividing the percentages by the respective atomic weights we get the ratio of the atoms to be *one* of nitrogen to *three* of hydrogen. Since one liter of ammonia weighs about 0.77 grams, the gram-molecular weight (that is, the weight of 22.4 liters) is 17.2. This corresponds to a formula NH_3.

We may write the equations for these reactions:

$$\underset{\text{copper oxide}}{3\,CuO} + \underset{\text{ammonia}}{2\,NH_3} \longrightarrow \underset{\text{copper}}{3\,Cu} + \underset{\text{water}}{3\,H_2O} + \underset{\text{nitrogen}}{N_2}$$

$$\underset{\text{magnesium}}{3\,Mg} + \underset{\text{ammonia}}{2\,NH_3} \longrightarrow \underset{\text{magnesium nitride}}{Mg_3N_2} + \underset{\text{hydrogen}}{3\,H_2}$$

$$\underset{\text{magnesium nitride}}{Mg_3N_2} + \underset{\text{water}}{6\,H_2O} \longrightarrow \underset{\text{magnesium hydroxide}}{3\,Mg(OH)_2} + \underset{\text{ammonia}}{2\,NH_3}$$

209. Laboratory preparation of ammonia. By heating a water solution of ammonia we can conveniently prepare the pure gas. When the solution is boiled, the dissolved gas is expelled because it is much less soluble in hot than in cold water. If we wish to free the gas of water vapor, we arrange the apparatus (Fig. 120) so that the ammonia passes up through a **drying tower** which is filled with pieces of soda lime (NaOH and CaO). Because of its extreme solubility in water the gas is collected in a bottle held mouth down, from which it displaces the air.

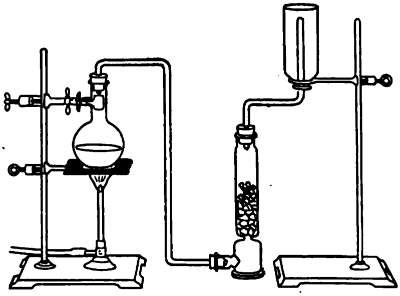


Fig. 120. Preparation of dry ammonia.

Another convenient way of preparing the gas is by heating a mixture of ammonium chloride, or sal ammoniac (NH_4Cl), and slaked lime ($Ca(OH)_2$) in a large test tube, as shown in figure 121. The reaction is as follows:

$$2\,NH_4Cl + Ca(OH)_2 \longrightarrow CaCl_2 + 2\,H_2O + 2\,NH_3 \uparrow$$

210. Properties of ammonia. Aside from its pungent odor the most striking characteristic of ammonia is its extreme solubility. It is even more soluble in water than hydrogen chloride.

The rapidity with which ammonia gas is absorbed by water may be shown by the following experiment. A large flask is entirely filled with ammonia, and a stopper is inserted through which runs a long tube and a " dropper " containing water. The lower end of the tube dips into a beaker which contains a red litmus solution (slightly acid). By pinching the rubber bulb a little water is ejected into the flask, whereupon the contents of the beaker at once rush up into the flask (Fig. 122) and the *red solution becomes blue.*

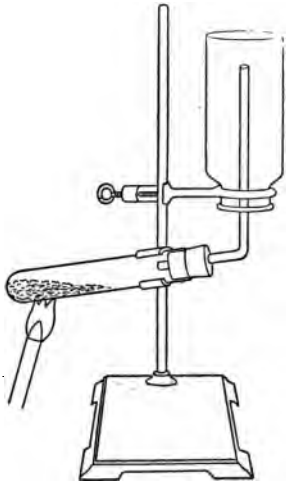


Fig. 121. Decomposition of ammonium chloride.

As might be supposed from its molecular weight, 17, ammonia is about one-half as heavy as air. It is easily liquefied; at ordinary temperatures a pressure of only about 4.5 atmospheres (66 pounds per square inch) is needed.

211. Refrigeration with liquid ammonia. Liquid ammonia is very extensively used in making artificial ice and in producing the low temperature required in cold-storage plants. This use of ammonia depends on the fact that it can easily be liquefied at ordinary temperatures by applying pressure, and that when this pressure is released the gas evaporates, absorbing a great deal of heat from the surroundings.

Figure 123 shows how this principle is applied in the production of artificial ice. The gas is compressed by pump *A* and is forced through the coil of pipe, where the heat produced by the compression is removed by running water. When the ammonia emerges from this coil, it is at room temperature and under sufficient pressure to be a liquid. The liquid ammonia flows through an expansion valve, which connects with the long series of coils; these are made of large pipe and are under atmospheric pressure. In these pipes the liquid now evaporates (because it is under atmospheric pressure), and in so doing it absorbs heat from the surrounding bath of brine. The gas is returned to the pump and again makes the cycle. The temperature of the brine is thus lowered to about –15° C. The brine, which is a solution of common salt or calcium chloride ($CaCl_2$), does not freeze at this temperature. Pure water in suitable metal containers is immersed in it and is frozen in from 24 to 36 hours into cakes of ice. Sometimes sulfur dioxide (SO_2) or carbon dioxide (CO_2) is used instead of ammonia.

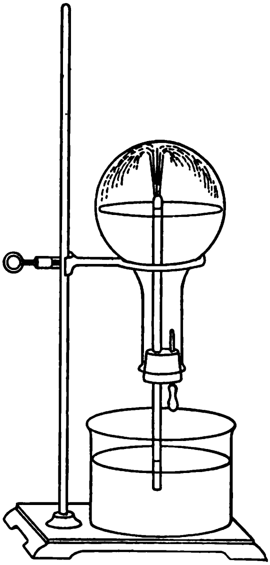


Fig. 122. Ammonia is extremely soluble in water.

If it is desired to keep the interior of a room at a low temperature, the brine itself is circulated by means of a pump through coils of pipe placed in the room; it then returns to the tanks

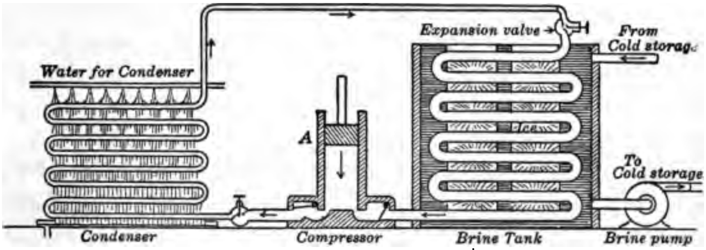


Fig. 123. Diagram of a refrigeration plant.

containing the ammonia coils. The temperature of a room can thus be kept very low, and meat and other food placed in it can be preserved for a long time, since at this low temperature decay and putrefaction practically cease (Fig. 124).

In many cities the entire ice supply is produced in plants using the ammonia process just outlined. Cold-storage plants which are cooled by ammonia refrigeration machines are located wherever convenient, in connection with the handling of food products. Thus many hotels and clubs have small ammonia refrigeration plants, which serve instead of the usual household ice chest, and most steamships are also equipped with them.

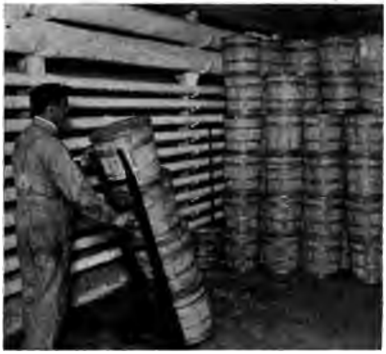


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Fig. 124. Inside view of a refrigeration room.

212. The manufacture of ammonia. Practically all of the ammonia that is sold is now obtained from coal. Coal is very largely composed of carbon, but it also contains some very complicated compounds, which were probably formed by plant life ages ago. When coal is heated in closed containers away from the air, these compounds decompose and produce a mixture of gases, water, and tar, while the carbon is left behind as coke. Under these conditions the nitrogen compounds in the coal produce ammonia, which is removed from the other gases by dissolving it in water. The production of coke and coal gas from coal is carried out on a large scale, thus making great quantities of ammonia available.

213. Making ammonia directly from the elements. It has long been known that if electric sparks are passed through a mixture of nitrogen and hydrogen, a small amount of ammonia can be produced by synthesis from the two elements. A process has recently been developed for combining these gases on an industrial basis. A mixture of nitrogen and hydrogen is subjected to a pressure of about 200 atmospheres, is heated to about 500° C., and then passed over finely divided iron, which acts as a catalyst. Only a small percentage of the gases unites to form ammonia; this small amount is absorbed in water, however, and the remaining mixture of gases again passes over the iron and the process is repeated.

In this so-called **Haber process** the nitrogen and hydrogen are prepared from producer gas (§ 255) and steam. Producer gas is essentially a mixture of nitrogen and carbon monoxide made by burning coal in a limited supply of air. This gas is mixed with steam and passed over a heated catalyst, which causes the carbon monoxide to react with the water as follows:

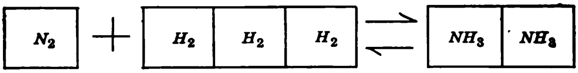
$$CO + H_2O \longrightarrow CO_2 + H_2$$

The resulting gas contains nitrogen (originally present in the air), hydrogen, and carbon dioxide. The latter compound is removed by treating the highly compressed gas with water. This process will be considered again in connection with the fixation of nitrogen.

214. Chemical behavior of ammonia. We have just seen that under certain conditions the inert element nitrogen will combine with hydrogen to form ammonia:

$$N_2 + 3\,H_2 \rightleftharpoons 2\,NH_3$$

One volume of nitrogen unites with *three* volumes of hydrogen to form *two* volumes of ammonia:



At ordinary temperatures ammonia is a stable compound, but when heated to high temperatures (above 700° C.) or when subjected to an electric discharge, it may be decomposed into its elements. Therefore we write the equation as a reversible one.

Ammonia will neither support combustion nor burn in air, but it can be made to burn in an atmosphere of oxygen with a feeble, yellowish flame. We have already observed (§ 208) that it acts as a reducing agent. The hydrogen of ammonia can be replaced by a few metals, forming the nitrides. Thus we have seen magnesium change into magnesium nitride (Mg_3N_2) when ammonia was passed over it.

215. Ammonium hydroxide. The action of ammonia upon water does not seem to be merely a solution of the gas in water since the resulting solution has basic properties. It turns red litmus blue; it feels soapy and slippery to the touch; it neutralizes acids, forming salts. Therefore it appears as though a part of the gas must combine chemically with water as indicated in the equation:

$$NH_3 + H_2O \rightleftharpoons NH_4OH$$

The product of the reaction is called **ammonium hydroxide,** and its solution contains the **ammonium ion** (NH_4^+) and the **hydroxyl ion** (OH^-). When this solution is heated, the compound decomposes into ammonia and water. Therefore the equation is written to represent a reversible reaction.

216. Ammonium salts. When ammonia and hydrogen chloride combine at ordinary temperatures, the product is a white crystalline solid called ammonium chloride (NH_4Cl):

$$NH_3 + HCl \longrightarrow NH_4Cl$$

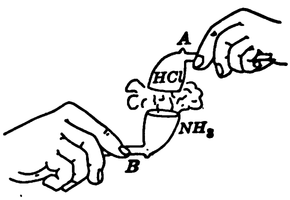


Fig. 125. Union of ammonia with hydrogen chloride.

This reaction can be shown very prettily by taking two clay pipes and moistening the inside of one with a concentrated water solution of ammonia and the other with concentrated hydrochloric acid. When the mouths of the two pipes are brought near each other, a white cloud of ammonium chloride particles is produced (Fig. 125). Enough of the gaseous ammonia and gaseous hydrogen chloride escape from the aqueous solution to cause this reaction to take place in the air surrounding the pipes.

When ammonium hydroxide is neutralized with hydrochloric acid and the solution is evaporated to dryness, a white solid results which is identical with that produced by the union of gaseous ammonia and hydrogen chloride. This is, of course, **ammonium chloride**, or **sal ammoniac**:

$$NH_4^+ + OH^- + H^+ + Cl^- \longrightarrow NH_4^+ + Cl^- + H_2O$$

Although the ammonium radical (NH_4) has never been obtained in a free state, yet we have many ammonium salts. In all of these compounds this group of atoms NH_4 acts very much like a monovalent metal, such as potassium or sodium. In a water solution these salts are ionized, giving NH_4 as the positive ion. Thus:

$$NH_4Cl \longrightarrow NH_4^+ + Cl^-$$

If, however, we send an electric current through such a solution, we do *not* obtain ammonium and chlorine, because the chlorine reacts with the solution, forming hydrochloric acid and nitrogen, and the ammonium ion decomposes into ammonia and hydrogen, the ammonia dissolving in water.

When ammonium salts are heated in a dry tube, they are decomposed and most of them give ammonia and an acid. For example,

$$NH_4Cl \rightleftharpoons NH_3\uparrow + HCl$$

It will be noticed that in this case both products are volatile, but when these products are cooled, they reunite to form the solid ammonium chloride. Here again we have a case of a reversible reaction.

In order to liberate ammonia from its salts, we have merely to heat any ammonium compound with an alkali (such as lime or sodium hydroxide) in order to neutralize the acid; we then get the unmistakable odor of free ammonia. This can be used as a **test for ammonium salts.**

217. Uses of ammonia. We have already seen that liquefied ammonia is used for refrigeration purposes, being shipped in strong steel cylinders. The aqueous solution, **aqua ammonia**, is used as a cleanser both in the home and in the industries. Ammonium sulfate ($(NH_4)_2SO_4$) is a valuable fertilizer since it contains a large percentage of nitrogen and, like all ammonium salts, is very soluble. Sal ammoniac (NH_4Cl) is used commercially in the manufacture of several types of batteries. **Smelling salts** are made of ammonium carbonate ($(NH_4)_2CO_3$), an unstable salt which decomposes into ammonia, water, and carbon dioxide:

$$(NH_4)_2CO_3 \longrightarrow 2\,NH_3\uparrow + H_2O + CO_2\uparrow$$

Lumps of the solid salt are covered with alcohol and some aromatic oil in order to make the powerful odor of the ammonia pleasanter. Ammonium nitrate (NH_4NO_3) is used in explosives because it decomposes easily and leaves no solid products.

SUMMARY OF CHAPTER XIX

AMMONIA (NH_3) is a colorless gas with a pungent odor, about half as heavy as air and exceedingly soluble in water. It is easily liquefied at ordinary temperatures.

In *nature* ammonia is formed by the putrefaction of animal and vegetable matter. In the *laboratory* it is usually prepared by heating ammonia water or a mixture of ammonium chloride and calcium hydroxide. The chief *commercial* source is from the distillation of coal. In the *Haber process* nitrogen and hydrogen combine directly to form ammonia.

CHEMICAL BEHAVIOR: ammonia *reduces copper oxide* to copper, forming water and nitrogen; ammonia reacts with hot magnesium, producing magnesium nitride and hydrogen; ammonia combines with hydrogen chloride to form ammonium chloride.

AMMONIA IN WATER SOLUTION is basic and contains the NH_4^+ and OH^- ions of *ammonium hydroxide.*

AMMONIUM SALTS are prepared by neutralizing ammonium hydroxide with acids.

AMMONIA IS USED for refrigeration purposes, as a cleansing agent (in water solution), and as a source of ammonium compounds.

QUESTIONS AND PROBLEMS

1. What is the difference between ammonia and ammonium?

2. What would be the action of dry ammonia on dry litmus paper? Why?

3. What three gases are sometimes used in refrigeration plants? What property have they in common?

4. How would you prove that ammonium hydroxide is a weak base?

5. Ammonia is sometimes spoken of as a basic anhydride. Explain.

6. What is meant by a reversible reaction? Give two examples from this chapter.

7. How would you test a salt for the presence of the ammonium radical?

8. Write the equation for the neutralization of ammonium hydroxide by sulfuric acid.

9. Ammonia is passed over hot copper oxide so as to produce 500 cc. of nitrogen. How many cubic centimeters of ammonia are required?

10. Ammonia is passed over hot magnesium so as to produce 1 liter of hydrogen. How many liters of ammonia are needed?

11. If 10 grams of magnesium nitride are put into water, how many grams of ammonia are produced?

12. If *aqua ammonia* is 35% by weight ammonia and has a density of 0.882 g. per cc., how many grams of ammonia are there in 100 cc. of the solution?

13. How many grams of ammonium chloride are required to react with slaked lime in order to give the ammonia required in Problem 12?

TOPIC FOR FURTHER STUDY

Refrigeration. If possible, visit a cold-storage warehouse or an artificial-ice plant. What is the principal expense entailed in this method of refrigeration? Investigate the household refrigerator. Measure the temperature in a household refrigerator with a thermometer. What is the temperature in a cold-storage plant? In an ice-cream freezer? On what principle do the iceless refrigerators operate? (*Cressy's* Discoveries and Inventions.)

CHAPTER XX

NITRIC ACID AND OXIDES OF NITROGEN

Saltpeter — nitric acid, preparation and properties — oxidizing agent — aqua regia — action with metals — nitrates — test for NO_3 ion — uses.

Oxides of nitrogen — nitric oxide — nitrogen dioxide — nitrous oxide.

218. Saltpeter. Saltpeter, or **niter**, is known to most people as one of the ingredients of gunpowder and as a preservative for meats. It was formerly obtained from certain dry countries in Asia where a decomposition product of animal matter reacted with potash to form potassium nitrate (KNO_3). Another similar compound, called **Chile saltpeter**, is found in great deposits in Chile and Peru (Fig. 126). This raw saltpeter, "caliche," contains from 17 to 50 per cent of sodium nitrate ($NaNO_3$).

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Fig. 126. Saltpeter fields in Chile.

As long ago as the ninth century men knew how to make **nitric acid** (HNO_3) from saltpeter. They followed a method similar to our own, and called the acid "aqua fortis" (strong water) because of its great chemical activity.

219. Preparation of nitric acid. Nitric acid is generally prepared by a process very like that used in the preparation of hydrochloric acid, namely, by the action of concentrated sulfuric acid on a nitrate. Sodium nitrate, as the most abundant of the nitrates, is mixed with concentrated sulfuric acid and heated in a retort. In the laboratory we take a tubulated glass retort (Fig. 127) for this purpose, but in the commercial manufacture of nitric acid an iron retort (Fig. 128) is used. The nitric acid is much more volatile than the sulfuric acid; hence it distills off and is condensed in a suitable apparatus. The substance left in the retort is sodium bisulfate:

$$NaNO_3 + H_2SO_4 \longrightarrow NaHSO_4 + HNO_3 \uparrow$$

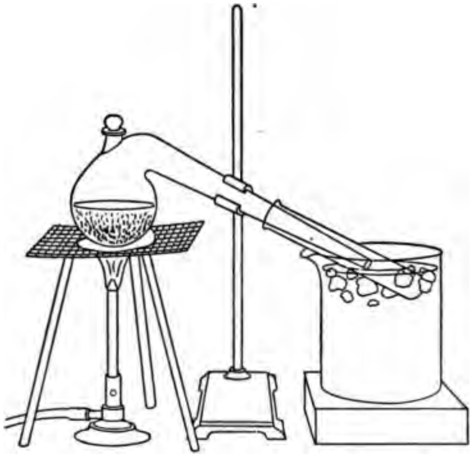

Fig. 127. Laboratory preparation of nitric acid.

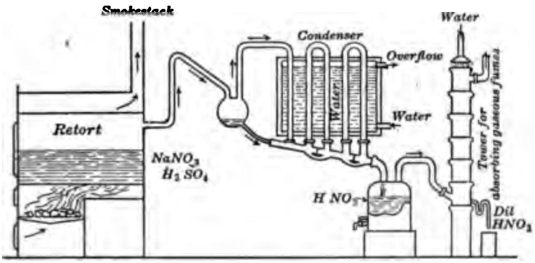

Fig. 128. Commercial preparation of nitric acid.

220. Properties. Pure nitric acid is a colorless liquid, boiling at 86° C. It fumes strongly when exposed to moist air. It is miscible with water in all proportions; the concentrated form which we buy contains about 68 per cent of the acid, the rest being water. Such a mixture has a density of 1.4 grams per cubic centimeter and boils at 120° C. It is highly corrosive, a few drops on the skin causing a bad burn. The dilute acid will turn the clothing and skin yellow.

Nitric acid can very easily be decomposed into water, nitrogen dioxide (NO_2), and oxygen. This decomposition takes place even when the acid is exposed for a long time to sunlight. When the acid is heated strongly the decomposition is very rapid:

$$4\,HNO_3 \longrightarrow 2\,H_2O + 4\,NO_2 + O_2$$

Nitrogen dioxide is a red-brown gas which dissolves in water. When it dissolves in nitric acid it gives the latter a yellow color. The so-called **fuming nitric acid** results if much of this oxide is dissolved.

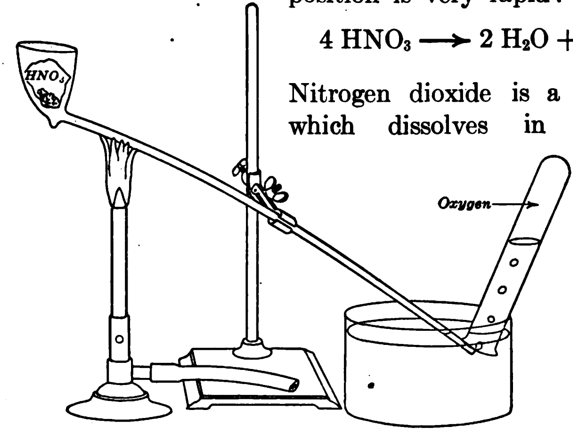

Fig. 129. Decomposition of nitric acid in a clay pipe.

We may show the decomposition of nitric acid by arranging a clay pipe so that the stem dips beneath the water, as in figure 129. When the stem is red-hot a few drops of concentrated nitric acid are poured into the bowl. As the acid runs down the stem, it is decomposed into water, oxygen, and nitrogen dioxide. This latter gas dissolves in water, and thus only oxygen is collected. The red-brown color which is characteristic of nitrogen dioxide can easily be seen when the bubbles first appear in the water.

221. Oxidizing action. Since nitric acid easily decomposes and gives off oxygen it is a good oxidizing agent. The equation which represents the decomposition of nitric acid when it acts as an oxidizing agent is as follows;

$$2\ HNO_3 \longrightarrow H_2O + 2\ NO + 3\ [O]$$

We indicate the fact that the oxygen is taken up by some other substance and not itself set free by writing the symbol in brackets.

The oxidizing action of nitric acid can be shown by gently heating a small quantity of sawdust and putting two or three drops of concentrated nitric acid on the charred mass. This experiment is best carried out in a crucible or porcelain dish (Fig. 130). The mass instantly takes fire, the charcoal burning at the expense of the oxygen from the nitric acid.

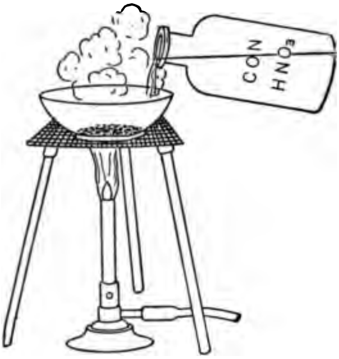

Fig. 130. Action of nitric acid on charred sawdust.

222. Aqua regia. Nitric acid oxidizes hydrochloric acid to water and free chlorine:

$$HNO_3 + 3\ HCl \longrightarrow 2\ H_2O + NO + 3\ [Cl]$$

For this reason a mixture of one part of nitric and three parts of hydrochloric acid slowly evolves free chlorine, which at the moment of its liberation is very active. This mixture of acids, called **aqua regia**, will dissolve gold and platinum. We speak of an element at the moment of its liberation from a compound as being in the **nascent state**; most elements in this state are more active than in the free state. The nascent state we shall indicate by writing a bracket around the symbol. Since we do not know the molecular condition of a nascent element, we write a monatomic formula for it.

223. Action with metals. Nitric acid behaves differently from most acids as regards its action with metals. Free hydrogen is practically never produced by the action of even dilute nitric acid on metals. The reason is that the hydrogen, which is probably at first produced, is immediately oxidized to water by the nitric acid, the acid in turn being reduced to oxides of nitrogen. The exact product of the reaction depends on the concentration of the acid and the particular metal employed. In some cases the oxides of nitrogen may be further reduced to ammonia by the nascent hydrogen.

The most typical reaction is that of moderately dilute nitric acid on copper. The products in this case are copper nitrate, water, and nitric oxide:

$$\underset{\text{copper}}{3\,Cu} + \underset{\substack{\text{nitric}\\ \text{acid}}}{8\,HNO_3} \longrightarrow \underset{\substack{\text{copper}\\ \text{nitrate}}}{3\,Cu(NO_3)_2} + \underset{\substack{\text{nitric}\\ \text{oxide}}}{2\,NO} + \underset{\text{water}}{4\,H_2O}$$

The balancing of this equation is difficult and it will be found best to memorize it.

224. The nitrates. Nitric acid is a monobasic acid and forms salts, called **nitrates**, when neutralized by a base. Thus:

$$Na^+ + OH^- + H^+ + NO_3^- \longrightarrow Na^+ + NO_3^- + H_2O$$

Besides dissolving all metals except gold and platinum, it dissolves a number of metallic oxides, such as copper oxide, forming the corresponding nitrate and water:

$$\underset{\substack{\text{copper}\\ \text{oxide}}}{CuO} + \underset{\substack{\text{nitric}\\ \text{acid}}}{2\,HNO_3} \longrightarrow \underset{\substack{\text{copper}\\ \text{nitrate}}}{Cu(NO_3)_2} + \underset{\text{water}}{H_2O}$$

Nitric acid acts on such salts as will give a volatile product with the acid:

$$\underset{\substack{\text{calcium}\\ \text{carbonate}}}{CaCO_3} + \underset{\substack{\text{nitric}\\ \text{acid}}}{2\,HNO_3} \longrightarrow \underset{\substack{\text{calcium}\\ \text{nitrate}}}{Ca(NO_3)_2} + \underset{\text{water}}{H_2O} + \underset{\substack{\text{carbon}\\ \text{dioxide}}}{CO_2\uparrow}$$

Nitrates cannot be prepared by precipitation because the *nitrates of all metals are soluble in water.* We therefore often use the nitrate of a metal when we wish to work with a water solution containing the ion of that metal.

When a nitrate is heated, it generally decomposes into the metallic oxide, nitrogen dioxide, and oxygen:

$$\underset{\substack{\text{copper}\\\text{nitrate}}}{2\,\mathrm{Cu(NO_3)_2}} \longrightarrow \underset{\substack{\text{copper}\\\text{oxide}}}{2\,\mathrm{CuO}} + \underset{\substack{\text{nitrogen}\\\text{dioxide}}}{4\,\mathrm{NO_2}} + \underset{\text{oxygen}}{\mathrm{O_2}}$$

But in the case of sodium and potassium nitrates the products are oxygen and a **nitrite**:

$$\underset{\substack{\text{sodium}\\\text{nitrate}}}{2\,\mathrm{NaNO_3}} \longrightarrow \underset{\substack{\text{sodium}\\\text{nitrite}}}{2\,\mathrm{NaNO_2}} + \underset{\text{oxygen}}{\mathrm{O_2}}$$

225. Test for nitrates. We may easily recognize a nitrate by adding concentrated sulfuric acid and then heating with copper. The nitric acid which is formed acts on the copper, and *brown vapors appear*. Minute amounts of the NO_3 ion may be detected by adding a solution of ferrous sulfate ($FeSO_4$) to the solution which is to be tested. Then concentrated sulfuric acid is poured in so as to form a layer below the mixed solutions. The *appearance of a dark brown ring* (Fig. 131) *just above the heavier sulfuric acid indicates the presence of the* NO_3 *ion.* The composition of this dark colored compound is not definitely known. The test, however, is very delicate, although it requires some skill in manipulation.

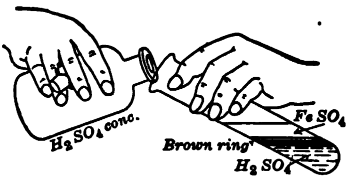

Fig. 131. **Dark brown ring indicates a nitrate.**

226. Uses. Nitric acid enters very extensively into the preparation of a number of organic compounds which are used as explosives and as intermediate substances in the preparation of dyes. The acid is also employed as a cleansing agent and for dissolving certain metals. The nitrates are very largely used as fertilizers. (See Industrial Chart, p. 205.)

227. Oxides of nitrogen. Five oxides of nitrogen are known; only three of these are important. They are nitrous oxide (N_2O), nitric oxide (NO), and nitrogen dioxide (NO_2). Nitrogen trioxide (N_2O_3) and nitrogen pentoxide (N_2O_5) are unstable substances of no especial importance.

228. Nitric oxide (NO). Nitric oxide is most readily prepared by the action of dilute nitric acid upon copper. The equation for this reaction has already been discussed (§ 223). The apparatus is the same as that used to generate hydrogen. The gas is colorless and almost insoluble in water.

The most important property of nitric oxide is its ability to unite with oxygen, even at ordinary temperatures, to form a red-brown gas, nitrogen dioxide (NO_2):

$$\underset{\text{nitric oxide}}{2\,NO} + \underset{\text{oxygen}}{O_2} \longrightarrow \underset{\text{nitrogen dioxide}}{2\,NO_2}$$

229. Nitrogen dioxide (NO_2). This gas, which is formed when nitric oxide comes in contact with oxygen, has a very unpleasant odor and is poisonous when inhaled.

We may prepare nitric oxide as just described, fill a tube with it over water, and then introduce oxygen (Fig. 132), which can be conveniently generated by dropping water on sodium peroxide (Na_2O_2). As each bubble of oxygen enters the tube, it unites with the nitric oxide to form the red-brown nitrogen dioxide. But the color soon fades, and the water rises in the tube as the dioxide reacts with the water.

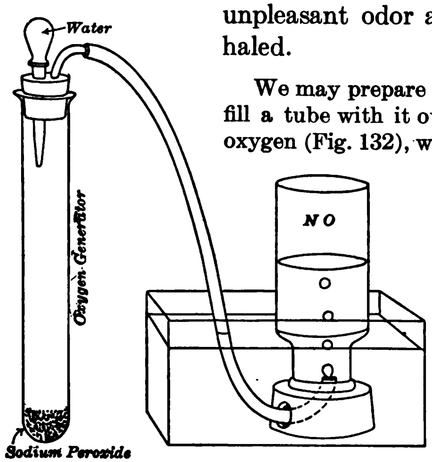

Fig. 132. Introducing oxygen into nitric oxide.

An interesting property of nitrogen dioxide is its reaction upon water by which nitric acid and nitric oxide are produced:

$$\underset{\text{nitrogen dioxide}}{3\,NO_2} + \underset{\text{water}}{H_2O} \longrightarrow \underset{\text{nitric acid}}{2\,HNO_3} + \underset{\text{nitric oxide}}{NO}$$

When cooled this gas grows pale yellow, and its density *becomes twice as great.* This paler gas has the formula N_2O_4

and is called nitrogen tetroxide. At ordinary temperatures the gas is a mixture of the two; so we express the relation by a reversible equation:

$$\underset{\substack{\text{high}\\\text{temperatures}}}{2\,NO_2} \rightleftharpoons \underset{\substack{\text{low}\\\text{temperatures}}}{N_2O_4}$$

We have already seen that nitrogen dioxide plays the part of the carrier of oxygen in the manufacture of sulfuric acid by the chamber process (§ 200).

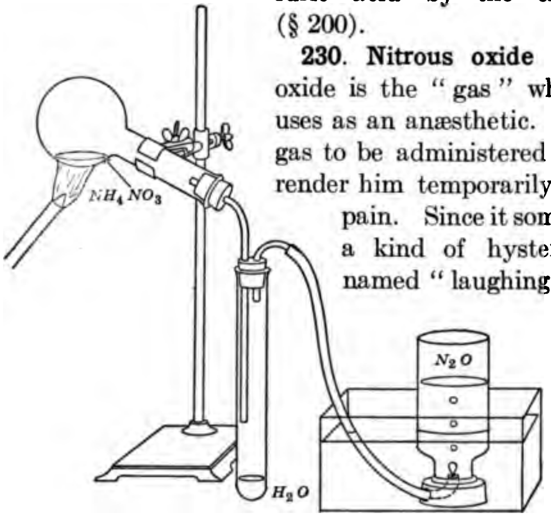

Fig. 133. Preparation of nitrous oxide.

230. Nitrous oxide (N_2O). Nitrous oxide is the "gas" which the dentist uses as an anæsthetic. It was the first gas to be administered to a patient to render him temporarily unconscious of pain. Since it sometimes produces a kind of hysteria it has been named "laughing gas."

It can be conveniently prepared by heating ammonium nitrate. This decomposes into water and nitrous oxide:

$$\underset{\substack{\text{ammonium}\\\text{nitrate}}}{NH_4NO_3} \longrightarrow \underset{\text{water}}{2\,H_2O\uparrow} + \underset{\substack{\text{nitrous}\\\text{oxide}}}{N_2O\uparrow}$$

The apparatus may be set up as shown in figure 133. The heat must be carefully regulated or an explosion may occur. The nitrate first melts and then begins to effervesce as it decomposes. One of the products is steam, which is condensed in the catch bottle; the other, nitrous oxide, is collected over warm water, in which it is but slightly soluble.

Nitrous oxide is a colorless gas with a slightly sweet taste. It supports combustion almost as well as oxygen. Unlike oxygen, however, it does not unite with nitric oxide to form the brown dioxide. It will not support the combustion of sulfur unless it is burning vigorously. Nitrous oxide is easily liquefied and in this form is sold in steel cylinders. When it is used in minor operations, it is customary to mix it with air in order not to deprive the patient entirely of oxygen.

It will be well to compare the action of heat on ammonium nitrate and on ammonium nitrite:

$$\underset{\text{ammonium nitrite}}{NH_4NO_2} \longrightarrow \underset{\text{water}}{2\,H_2O} + \underset{\text{nitrogen}}{N_2}$$

This was the reaction which we used in preparing pure nitrogen (§ 75).

SUMMARY OF CHAPTER XX

NITRIC ACID IS MADE by heating concentrated sulfuric acid and sodium nitrate. It is a colorless liquid which mixes with water. The commercial concentrated acid contains 32 per cent of water.

NITRIC ACID is easily decomposed, forming oxides of nitrogen and free oxygen. It is a powerful *oxidizing agent.* A mixture of nitric and hydrochloric acid is *aqua regia;* this furnishes nascent chlorine.

UNLIKE MOST ACIDS nitric acid very seldom produces free hydrogen with metals. *Oxides of nitrogen* are usually the products; in some cases ammonia may be formed.

NITRATES MAY BE PREPARED by the action of nitric acid on —

(1) metals, except gold and platinum;
(2) oxides and hydroxides;
(3) salts giving volatile products.

NITRIC ACID IS USED in the preparation of explosives, fertilizers, and dyes. Of the nitrates those of sodium and potassium are the most important. Sodium nitrite is made by heating sodium *nitrate.*

NITRIC OXIDE (NO) is prepared by the action of dilute nitric acid on copper. In contact with oxygen it produces *nitrogen dioxide* (NO_2), which is a red-brown gas, poisonous, and soluble in water. Nitrogen dioxide on cooling doubles its molecules and passes into *nitrogen tetroxide* (N_2O_4).

NITROUS OXIDE (N_2O) is made by heating ammonium nitrate. It supports combustion. It is used in surgery to produce anæsthesia.

Questions and Problems

1. Why are the deposits of Chile saltpeter so valuable?

2. Why is sodium nitrate instead of potassium nitrate used in the manufacture of nitric acid?

3. What is *aqua ammonia? aqua fortis? aqua regia?*

4. Explain how the chloride is formed when gold or platinum dissolve in aqua regia.

5. Name three metals which dissolve in nitric acid but do not dissolve in hydrochloric acid.

6. State the law which is illustrated in the oxides of nitrogen. Explain.

7. How would you distinguish nitrous oxide from oxygen?

8. How many grams of nitric acid could be made from 10 grams of sodium nitrate?

9. How many grams of nitric acid could be made from 10 grams of potassium nitrate? Compare this answer with that to Problem 8.

10. Calculate the density (grams per liter) of nitric oxide from the formula NO.

11. Compute the weight of copper which will be needed to generate with dilute nitric acid one liter of nitric oxide (standard conditions).

12. One liter of nitric oxide is converted into nitric dioxide by contact with the air. How many liters of air (approximately) will be required?

Topic for Further Study

Sodium nitrate from Chile. How is the material mined, purified, and shipped? How long will the present supply probably last? (*Duncan's* Chemistry *of Commerce.*)

CHAPTER XXI

EQUILIBRIUM; FIXATION OF NITROGEN

Reversible reactions — kinetic equilibrium — Law of Concentration, or Mass Action — effect of temperature — effect of catalysts.

Fixation of nitrogen — direct oxidation — ammonia process — cyanamide process. Explosives — nitrogen cycle — nitrogen compounds as fertilizers.

231. Reversible reactions. We have already met a number of reactions which will " work backwards " when the conditions are changed. We have called these **reversible reactions** and have indicated them by a double arrow. For example, when steam is passed over hot metallic iron, hydrogen is set free, and iron oxide is formed; but if hydrogen is passed over hot iron oxide, the oxide is reduced to iron, and water is formed:

$$\underset{\text{iron}}{3\,Fe} + \underset{\text{steam}}{4\,H_2O} \rightleftharpoons \underset{\substack{\text{iron}\\\text{oxide}}}{Fe_3O_4} + \underset{\text{hydrogen}}{4\,H_2}$$

In the first case we read the equation from left to right, and in the second case from right to left. In the first case we sweep out the hydrogen with a surplus of steam and prevent the reverse action; in the second case we sweep out the steam with a surplus of hydrogen.

Another example of a reversible reaction is the case of hydrochloric acid. In a normal solution (that is, one containing 36.5 grams HCl per liter) about 78 per cent of the molecules are ionized, and the rest are in the molecular state. This condition we represent by the following equation:

$$HCl \rightleftharpoons H^+ + Cl^-$$

If we add water and make the solution more dilute, more molecules dissociate, and the reaction goes from left to right; but if we evaporate the solution, the ions combine, and the reaction goes from right to left.

232. Kinetic equilibrium. In the first example we might inclose some iron turnings and steam in *a closed tube* and keep the temperature high enough for either reaction to go on. If we should keep the tube in this condition for some time and then should open it, we should find that no progress had been made in either direction; some of the iron would be oxidized, and there would be a certain proportion of hydrogen and of steam. This balanced condition is not believed to be due to any cessation of chemical action, but rather to the fact that *both actions are going on at the same rate.* Therefore it is called **kinetic equilibrium.**

In the case of a solution of hydrogen chloride we believe that the molecules are moving about rapidly and are constantly splitting up into hydrogen ions and chlorine ions. At the same time these ions in their wanderings about the solution are meeting others with an opposite charge and are uniting to form molecules of hydrogen chloride. The result is that although the molecules are continually dissociating and associating again, yet the ratio between the ions and the molecules does not change so long as the volume of the solution and its temperature remain constant. This, then, is another case of kinetic equilibrium.

We must *not conceive of kinetic equilibrium as a condition of rest.* It may help us to grasp the idea if we think of a tank which has water pumped in and flowing out at such a rate that it stays just three-fourths full. The *level of the water remains constant,* but the *actual water is continually changing.* This is a mechanical analogue of kinetic equilibrium.

233. Law of Concentration. In practical chemical work we usually want our *reactions to continue in one direction* until we obtain as much of the product as possible. Therefore it is necessary to study all the conditions of equilibrium and especially the **effect of concentration.** We can cause a reaction which is in equilibrium to go on further in one direction or the other by increasing the concentration of one of the substances in the reaction mixture. By concentration we mean simply the amount of material in a given volume.

If in the case of the equilibrium in the closed tube containing iron and steam we should open the tube and allow some of the hydrogen to escape, more would be formed, and the reaction would go from left to right; but if only the steam were permitted to leave the tube, then the hydrogen would go on acting with the oxide to restore the proportion, and the reaction would go from right to left. The continuance of the reaction in one direction or the other depends on the relative amounts in a given volume of the active substances, hydrogen and steam; that is, on their **concentration.** This is sometimes called the **Law of Mass Action.**

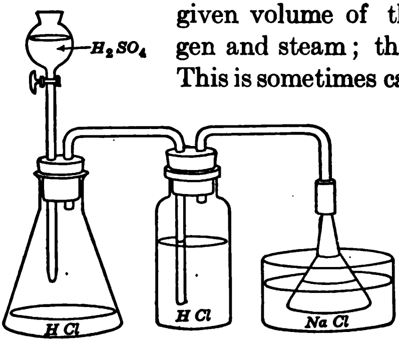

Fig. 134. Pure salt precipitated by hydrogen chloride.

To illustrate the application of this law to solutions, we place some saturated sodium chloride solution in a crystallizing dish. We then introduce hydrogen chloride gas through an inverted funnel (Fig. 134). After a short time crystals of sodium chloride are formed in the saturated solution.

In the saturated salt solution we have a case of equilibrium between the ions and the molecules of salt:

$$NaCl \rightleftharpoons Na^+ + Cl^-$$

When we introduce hydrogen chloride gas we add another case of equilibrium:

$$HCl \rightleftharpoons H^+ + Cl^-$$

We have *increased the concentration of the chlorine ions,* which means that the sodium ions meet the chlorine ions more frequently than before, and therefore they combine to form molecules of salt faster than the molecules dissociate. But the solution already is saturated with molecules of salt; hence salt crystallizes out as **pure sodium chloride.**

We may generalize these facts into the **Law of Concentration,** or **Mass Action,** as follows:

By increasing the concentration of one of the reacting substances or by decreasing the concentration of one of the products, we may cause the chemical action to go more nearly to completion in a given direction.

234. Applications of the Law of Concentration. We have already seen that a *reaction will go to an end* —

(1) if one of the products is *volatile:*

$$NaCl + H_2SO_4 \longrightarrow NaHSO_4 + HCl \uparrow$$

(2) if one of the products is *insoluble:*

$$NaCl + AgNO_3 \longrightarrow NaNO_3 + AgCl \downarrow$$

(3) if one of the products *does not ionize:*

$$NaOH + HCl \longrightarrow NaCl + H_2O$$

All neutralization reactions go to an end because water, which is always one product, is practically nonionized.

In each of these cases we see that the *action goes to completion because one of the products is removed;* that is, its concentration becomes practically zero.

Many reactions, however, do not go quite to an end because *no product is absolutely insoluble.* Take, for example, the reaction

$$Ba(NO_3)_2 + H_2SO_4 \longrightarrow BaSO_4 \downarrow + 2\ HNO_3$$

The barium sulfate is practically insoluble but not quite so. If we wish to precipitate all of the barium from a solution we add an excess of sulfuric acid. In this way we increase the concentration of the SO_4^{--} ions and so precipitate the Ba^{++} ions more completely.

In the experiments on combustion we found that charcoal and other materials burn faster in pure oxygen than in air (which is oxygen diluted with nitrogen). In a steamship the coal is burned under forced draft in order to supply the oxygen faster; that is, to increase the amount of oxygen available at any one time. According to the Law of Concentration, or Mass Action, we express these facts by stating that the *speed at which a given material burns depends for one of its factors upon the concentration of the oxygen.*

235. Effect of temperature. We have already seen many cases in which an increase in the temperature hastens a chemical reaction. It has been found that, in general, a rise of 10° C. about doubles the speed of most reactions.

FOR EXAMPLE, the directions on a Kodak Development Tank state that when the solution is 70° F., the time needed to develop a photographic film is 15 minutes; at 65° F., 20 minutes; at 60° F., 25 minutes; and at 55° F., 30 minutes. This means that raising the temperature of the developer 15 degrees Fahrenheit (or 8.3° centigrade) makes it work twice as fast.

The condition of equilibrium of any chemical reaction depends on the temperature. A change in temperature will almost always cause the equilibrium to shift in one direction or the other. This has been shown in the following equation:

$$\underset{\text{high temperatures}}{2\,NO_2} \rightleftharpoons \underset{\text{low temperatures}}{N_2O_4}$$

A rise in temperature favors the formation of the nitrogen dioxide from the nitrogen tetroxide with a corresponding increase in color. On cooling again the nitrogen dioxide goes back to the tetroxide and the color fades. *For every temperature there is a certain ratio between the amounts of these two oxides.*

236. Effect of catalysts. Many reactions do not come to equilibrium as quickly as in the case just discussed. For example, a mixture of nitrogen and hydrogen will stand at 500° C. and no change will take place. If, however, we pass this mixture of gases at the same temperature over finely divided iron, the reaction follows at once, and 3 per cent of ammonia is formed:

$$N_2 + 3\,H_2 \rightleftharpoons 2\,NH_3$$

A catalyst will thus increase the speed of a reaction and cause it to reach rapidly a condition of equilibrium. As pointed out before, it acts as a chemical lubricant, overcoming a certain amount of hindrance to the action. *A catalyst will not, however, change the equilibrium of a reaction.* We can find no catalyst which will cause nitrogen and hydrogen to combine to a greater extent than they do in the presence of heated iron.

FIXATION OF NITROGEN

237. The problem of fixation of nitrogen. Nitric acid and the nitrates are important in our modern life because they are necessary in the manufacture of **explosives** and of **fertilizers.** The principal source of nitric acid and the nitrates was formerly the deposits of sodium nitrate in Chile. This supply is not only rapidly becoming exhausted, but it may at any time be cut off from the rest of the world through some such contingency as war. The atmosphere, however, contains enormous quantities of nitrogen from which it should be possible to synthesize nitric acid and its derivatives. In fact, a number of successful methods have been developed for doing this very thing; they are called processes for the **fixation of nitrogen.** We shall consider three of the most important of these and shall find that what we have just learned about reversible reactions will be of great value in understanding them.

238. Direct oxidation. Nitrogen and oxygen will combine to a very slight extent at a very high temperature. The reaction is a reversible one and proceeds to the right as the temperature is increased:

$$N_2 + O_2 \rightleftharpoons 2\,NO$$

At 2000° C. only about one per cent of the mixed gases combine; at 3000° C. about five per cent; while at ordinary temperatures the equilibrium mixture contains practically no oxide. If the mixture of nitrogen and oxygen is heated to 3000° C. and is then allowed to cool down slowly to room temperature, there will be no apparent change. The nitric oxide which was formed at the high temperature will keep reverting to its elements as the temperature is gradually lowered. If, however, the mixture is *quickly cooled,* the reaction does not have time to reverse itself completely, and a certain amount of nitric oxide will be left. A number of commercial processes for directly oxidizing atmospheric nitrogen are based on this principle (Fig. 135). In all of these processes air is blown through a flame produced between the electrodes of a powerful electric arc. In passing through this arc the air reaches a high temperature and is then suddenly cooled as it leaves the flame. The gas from such a furnace contains about one per cent of nitric oxide. Since there is an excess of oxygen from

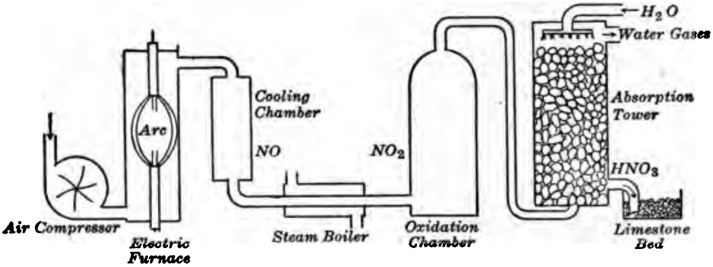

Fig. 135. Diagram of the Birkland-Eyde process of fixation of nitrogen.

the air in this mixture, the nitric oxide goes into nitrogen dioxide as the gas is cooled:

$$N_2 + O_2 \longrightarrow 2\,NO\text{; high temperature}$$

$$2\,NO + O_2 \longrightarrow 2\,NO_2\text{; lower temperature}$$

The gases are now led through towers down which water drips, and the nitrogen dioxide combines with the water, forming nitric acid and nitric oxide. The latter comes in contact with air and produces more nitrogen dioxide, which in turn reacts with the water. Thus, in the presence of air nitric oxide will completely dissolve in water, forming nitric acid:

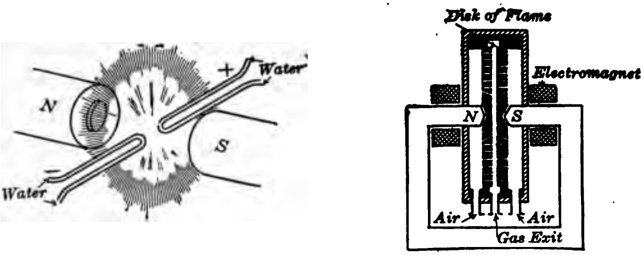

Fig. 136. Electric-arc furnace used to fix nitrogen.

$$3\,NO_2 + H_2O \longrightarrow 2\,HNO_3 + NO$$

$$2\,NO + O_2 \longrightarrow 2\,NO_2$$

$$4\,NO_2 + 2\,H_2O + O_2 \longrightarrow 4\,HNO_3$$

This nitric acid is neutralized with calcium carbonate, forming calcium nitrate, which is used chiefly as a fertilizer and as a source of nitric acid.

This method of making nitric acid (known as the Birkland-Eyde process) has worked successfully in Norway, where electric power is cheap on account of the abundant water power. The Birkland-Eyde electric furnace (Fig. 136) uses an electromagnet to spread out the arc into a disk of flame.

239. Ammonia process. We have already seen (§ 213) that ammonia can be prepared according to the Haber process by combining hydrogen with the nitrogen of the air. Nitric acid can then be made by the oxidation of the ammonia, which is done by heating a mixture of ammonia and air in contact with some catalyst, such as platinum. This process works at a relatively low temperature and therefore requires very little energy.

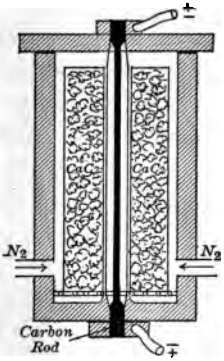

Fig. 137. Calcium cyanamide furnace.

240. Cyanamide process. There is another ammonia process which is not so direct. Calcium carbide (CaC_2), which is used to generate acetylene, will combine with nitrogen when heated (Fig. 137), forming carbon and a compound called calcium cyanamide ($CaCN_2$):

$$CaC_2 + N_2 \longrightarrow CaCN_2 + C$$

When this compound ($CaCN_2$) is treated with steam under pressure, it decomposes, forming calcium carbonate and ammonia:

$$CaCN_2 + 3\,H_2O \longrightarrow CaCO_3 + 2\,NH_3 \uparrow$$

The ammonia is oxidized into nitric acid, as described in the preceding section, according to the following reaction:

$$NH_3 + 2\,O_2 \longrightarrow HNO_3 + H_2O$$

The preparation of nitric acid from sodium nitrate is ordinarily the most economical process, but the newer methods of making it from atmospheric nitrogen are coming into use.

241. Explosives. An explosion is a very rapid chemical action in which a large volume of hot gases is produced from liquid and solid materials called **explosives**. The more rapid the action and the greater the quantity of gases produced, the more violent is the explosion.

All modern explosives contain nitrogen and are prepared from nitric acid. Old-fashioned **black powder** is a mixture of charcoal, sulfur, and potassium nitrate. On being ignited it burns suddenly with the evolution of a large volume of gases.

Place a small pile of gunpowder on a brick; then bring the ends of two wires which are connected to the secondary of a small induction coil almost together and embed them in the powder. When the electric spark is discharged between the wires, the powder burns with a huge puff of smoke (Fig. 138).

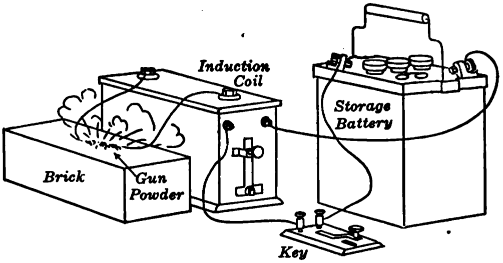

Fig. 138. Gunpowder exploded by an induction coil.

If this action occurs in a confined space, such as a gun barrel, a strong expansive force is exerted.

Modern explosives are carbon compounds which contain nitrogen and oxygen. They are formed by the action of nitric acid on a number of different substances. They all have the property of decomposing quickly when they are ignited, or when another explosive is set off very near them. This latter process is called **detonation.** When they decompose *they produce an enormous volume of gases at a high temperature,* and these gases exert a terrific pressure, which does the work required of an explosive.

The explosive which forms the basis of the **smokeless powder** used in guns of all calibers is made by the action of nitric acid on cotton. Cotton is a compound of carbon, hydrogen, and oxygen, called cellulose, and the action of the nitric acid converts it into a compound called **nitrocellulose.** The nitrocellulose is turned into a jelly-like mass by certain solvents; this is pressed out into short rods or strips and dried. It burns in the barrel of a gun when ignited by the priming charge, the gases produced push out the projectile (Fig. 139). **Trinitrotoluene (T.N.T.)** and **picric acid** are the explosives used inside high-explosive shells, in mines, and in depth charges; they are produced by the action of nitric acid on toluene and carbolic acid respectively. These latter substances are prepared from coal tar. Trinitrotoluene (T.N.T.) and picric acid can be set off only by first exploding in them a more sensitive explosive (a detonator). They explode suddenly and with much violence, causing great damage.

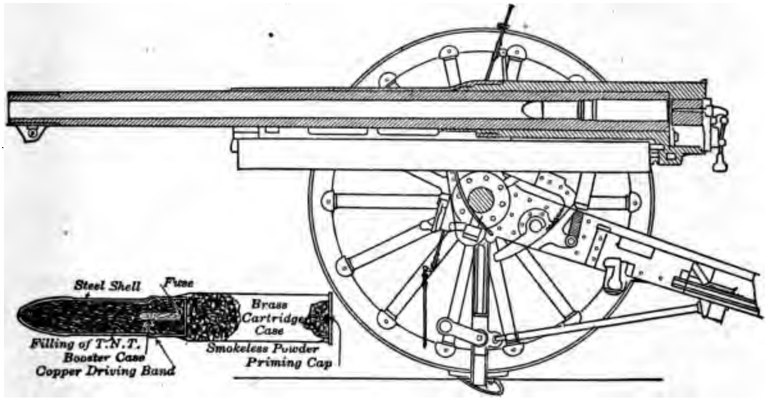

Fig. 139. Modern projectile used in the famous French 75 mm. gun.

Nitroglycerin is made by the action of nitric acid on glycerin $(C_3H_5(OH)_3)$. It is a very sensitive explosive and is little used unmixed. When it is soaked up in sawdust or some other porous material, and mixed with sodium nitrate, **dynamite** is produced. Dynamite is too violent and sensitive an explosive to be used in guns or shells. It is used for blasting, for making large holes in the earth, and for wrecking purposes both in war and peace. It is extensively used in modern agriculture for blasting out stumps (Fig. 140), breaking up bowlders, blasting ditches, as well as in preparing the holes for the planting of trees.

All modern warfare is based on the prodigious use of explosives of all kinds, which in turn depend for their manufacture on nitric acid. A belligerent country shut off from the supply of Chile saltpeter must have some method of producing nitric acid from the air or else have large stocks of saltpeter stored up. In the recent great war Germany was able to continue fighting, only because her chemists had perfected the processes for the production of nitric acid from the air.

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Fig. 140. Getting a stump ready for blasting.

242. Nitrogen cycle in nature. Nitrogen compounds are an essential part of all living plants and animals. Those nitrogen compounds which occur naturally are called proteins; they are composed of carbon, nitrogen, oxygen, and hydrogen. The plant is able to build them up from the water, carbon dioxide, and the inorganic nitrates which it finds in the soil. The protein in animals is obtained entirely from the plants or other animals which they consume. The waste products of plant and animal life contain the nitrogen of the original protein combined in a number of different compounds, which are easily acted upon by certain bacteria in the soil, forming ammonium compounds. These ammonium compounds in turn are oxidized by other bacteria to nitrates, which can be taken up by plants (Fig. 141).

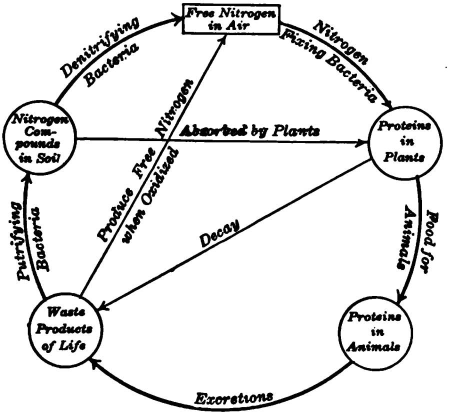


Fig. 141. Nitrogen cycle.

Thus nitrogen makes a **cycle** through plant and animal life and the soil.

243. Nitrogen compounds as fertilizers. Unfortunately there are two factors at work upsetting this cycle. In the first place, there are certain bacteria which convert some of the nitrates of the soil into free nitrogen, which is thus lost. In the second place, in modern civilization the waste products of plant and animal life no longer find their way back to the soil; large quantities of them are forever wasted by being dumped into rivers and the sea. For these reasons nitrogen must be continually supplied to the soil in some form in which the plants can use it. If the waste products of life, such as manure, are available, they make an excellent fertilizer, but the supply is very limited. The artificial fertilizers which can be prepared by the chemist consist of ammonium compounds and the nitrates. Most of the nitric acid produced by the direct oxidation of nitrogen is converted into calcium nitrate, which is used directly as a **fertilizer**. In some localities calcium cyanamide can be used directly as a nitrogen fertilizer. The ammonia prepared from it, or prepared by the Haber process, can be used as ammonium salts, or it may be oxidized to nitric acid and used as nitrates. *This problem of obtaining available nitrogen for plants from the atmosphere is one which will have great economic importance in the years to come.*

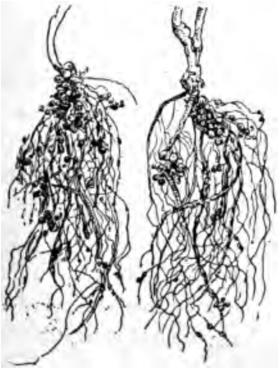


Fig. 142. Nodules containing nitrogen-fixing bacteria.

Some plants have themselves the power of converting the nitrogen of the air into useful compounds. This is brought about by certain bacteria which are found in the tubercles on the roots of leguminous plants, such as peas and clover (Fig. 142). It is now possible to buy these bacteria and to inoculate beans and similar plants with them before planting. This insures the growth of the bacteria on the roots of the plant and consequently the direct production of a nitrogen fertilizer by the plant itself.

SUMMARY OF CHAPTER XXI

REVERSIBLE REACTIONS come to a condition of *equilibrium* in which the two opposite reactions proceed at the same rate, and the average percentage composition of the mixture remains constant.

THE LAW OF CONCENTRATION, OR MASS ACTION, states that by increasing the concentration of one of the reacting substances or by decreasing the concentration of one of the products a reaction may go more nearly to completion in a given direction.

THE COMPOSITION OF THE EQUILIBRIUM MIXTURE depends on the temperature. A *catalyst* may be used to increase the speed of the reaction and cause the equilibrium to be established quickly, but it does not change the composition of the equilibrium mixture.

THE FIXATION OF NITROGEN means the process of manufacturing nitrogen compounds out of the free nitrogen of the air.

THE COMMERCIAL PROCESSES for the fixation of nitrogen include the following:

(1) the direct oxidation (Birkland-Eyde);
(2) the synthesis of ammonia (Haber);
(3) the cyanamide process.

The ammonia made in these last two processes can be oxidized to nitric acid.

NITRIC ACID is used in the manufacture of all *explosives. Smokeless powder* is nitrocellulose and is made from cotton. The bursting charge in shells, mines, etc., is *trinitrotoluene* (T.N.T.) or *picric acid. Dynamite* is nitroglycerin absorbed in some porous material and mixed with sodium nitrate.

NITRATES are essential to plant growth. Nitrogen goes through a *cycle* in animal and plant life and the soil. This cycle is upset by several factors. For this reason nitrates must be applied to the land as *fertilizers.*

QUESTIONS

1. Write the reaction of zinc oxide on carbon monoxide as a reversible reaction. State how the direction may be controlled.

2. Write the reaction of ammonia and water as a reversible reaction. State the conditions which control its direction.

3. Write the reaction for the decomposition of the red oxide of mercury. Under what conditions is this reaction reversible?

4. Why is chemical equilibrium considered kinetic?

5. State the Law of Concentration, or Mass Action. Why is it important to the industrial chemist?

6. What is meant by saying that a reaction goes to an end?

7. State three conditions under which reactions do go to an end. Illustrate by equations.

8. Examine the following reactions and write the complete equations for those which go to an end. State the reason in each case.

$$NaCl + Pb(NO_3)_2 \longrightarrow ?$$
$$NaNO_3 + CuSO_4 \longrightarrow ?$$
$$BaCl_2 + KNO_3 \longrightarrow ?$$
$$ZnCl_2 + AgNO_3 \longrightarrow ?$$
$$CaCO_3 + HCl \longrightarrow ?$$
$$FeS + H_2SO_4 \longrightarrow ?$$
$$KOH + HNO_3 \longrightarrow ?$$
$$Pb(NO_3)_2 + H_2SO_4 \longrightarrow ?$$
$$NaNO_3 + K_2SO_4 \longrightarrow ?$$
$$ZnSO_4 + HNO_3 \longrightarrow ?$$

9. Why are catalysts so commonly used in commercial chemical processes?

10. Why is the "*fixation of nitrogen*" such an important chemical problem?

11. When black gunpowder is ignited, the reaction may be expressed in the following equation:

$$2\,KNO_3 + 3\,C + S \longrightarrow K_2S + 3\,CO_2 + N_2$$

What are the approximate proportions in which the three components of gunpowder are mixed?

12. What per cent of the products in the equation just given are gases?

13. What other elements besides nitrogen are essential to plants?

14. How does a plant get its supply of nitrogen?

15. How does an animal get its supply of nitrogen?

16. Name and give the formulas for four fertilizers containing nitrogen.

17. What sort of plants can " fix " atmospheric nitrogen?

18. " Sulfate of ammonia " is a very concentrated commercial fertilizer. What per cent of nitrogen does it contain?

TOPICS FOR FURTHER STUDY

The fixation of nitrogen in the United States. What methods of fixing nitrogen are commercially possible to-day? What methods have been used on a large scale in this country? Why is the manufacture of nitrogen compounds from the air of national importance? (*Slosson's* Creative Chemistry, *Duncan's* Chemistry of Commerce, *U. S. Dept. of Commerce Bulletin No. 52* — Utilization of Atmospheric Nitrogen, and *Findlay's* Chemistry in the Service of Mankind.)

Explosives. Why are nitric and sulfuric acids considered the prime essentials for the manufacture of explosives? What other materials are needed for war-time explosives? for commercial explosives? What is the difference in action between smokeless powder, T.N.T., mercury, fulminate, and dynamite? How is each made? What explosives are used in mining and agriculture? (*Martin's* Modern Chemistry, *Tilden's* Chemical Discovery and Invention, and *Bird's* Modern Science Reader.)

CHAPTER XXII

CARBON, HEAT, AND FUELS

Carbon, its allotropic forms — diamond and graphite — coal, coke, lampblack, and boneblack — chemical behavior of carbon — coal as fuel — heat units — calorimeter — fuels and smoke — petroleum, gasolene, kerosene, oils — fuel gases: natural, coal, water, and producer — gas burners and flames — acetylene welding.

244. Carbon, a very important element. Carbon is a most interesting and unusual element, both in itself and in its compounds. We shall therefore have occasion to devote some time to its consideration. In this chapter we shall study the element itself and a few of its compounds with hydrogen, which are used as fuels. In Chapters XXIII and XXIV we shall go on with other important carbon compounds, both simple and complex. Its two oxides — carbon dioxide and monoxide — we have described in earlier chapters; we have already spoken of its essential importance to both plant and animal life. In general we may say the following of this element: that it has the usual characteristics neither of a metal nor of a nonmetal; that it forms no salts which give a positive ion; and that the only acid which is produced from its oxide (carbonic acid) is a very weak one.

245. Allotropic forms. It certainly requires much imagination to believe without more ado that charcoal, graphite, and diamond are only different forms of one and the same element. But despite their widely divergent physical properties they are all elementary carbon, and we may prove this experimentally by showing that each of them will burn in oxygen and evolve carbon dioxide as the sole product. Just as in the case of sulfur, we have here two crystalline forms, **diamond** and **graphite**, as well as certain **amorphous**, or noncrystalline, forms, such as charcoal and lampblack. It is possible to change these forms into one another. Charcoal can be converted into graphite by heating it to a very high temperature. It is even possible to make very small diamonds artificially.

246. Crystalline carbon. In certain localities of South Africa, South America, and the East Indies **diamonds** are found in gravel deposits. In their native state they are not at all like the gems which the name suggests. They generally look like ordinary rough stones, hardly transparent, and with little appearance of being crystals. To make them into gems (Fig. 143) they are ground, or "cut," in such a way that they will reflect light from a number of different faces; that is, "sparkle" in the light.

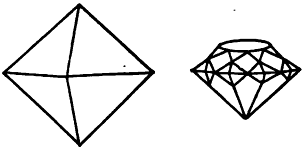


Fig. 143. Diamonds, rough and cut.

Diamond is one of the hardest substances known. It can be cut and polished only by other diamonds or by diamond powder. Some diamonds are brownish and even black; these are used for cutting glass and for giving a cutting edge to drills and rock-borers.

Another form of crystalline carbon is **graphite**. Although it occurs in nature abundantly in certain localities, it is now also manufactured on a large scale from hard coal. Hard coal is a form of impure carbon, which passes into graphite when it is subjected to a very high temperature out of contact with the air. This high temperature is produced in a so-called electric **resistance furnace**. A powerful electric current passes through a long bed of coal. Since coal is a poor conductor of electricity its resistance to the electric current produces large quantities of heat, which raise the mass to the desired temperature. The electric current plays no part in the chemical changes brought about in such a furnace but merely generates the necessary heat (Fig. 144).

Graphite is a glistening, black substance, which consists of a mass of fine, crystalline, slippery scales. It is soft and greasy and for this reason enters very extensively into the manufacture of lubricants. It is also used in making " lead " pencils, stove polishes, and paint. Crucibles are often made of it because it will not melt at the highest temperature. It is sometimes called **plumbago**, or **black lead.**

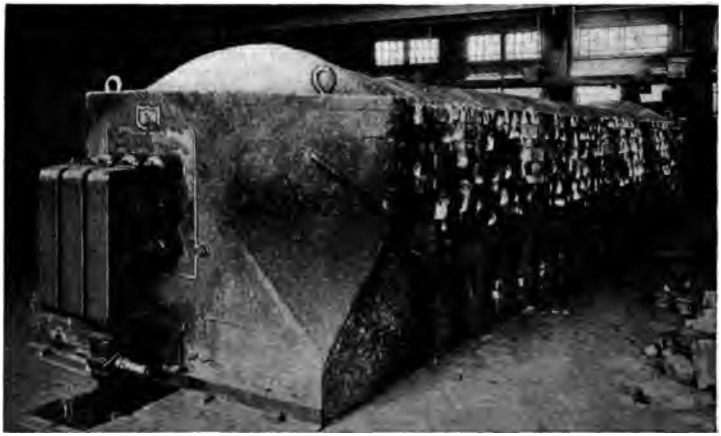


Fig. 144. Graphite electric furnace.

247. Amorphous carbon. The noncrystalline, or **amorphous,** form of carbon is prepared in many ways. Pure amorphous carbon can be got by heating cane sugar, which is a compound of carbon, hydrogen, and oxygen. On being heated the hydrogen and oxygen escape as water and leave the amorphous carbon. **Wood charcoal** is another form of amorphous carbon, but it contains a small amount of impurities as ash. It is made by heating wood out of contact with the air, a process which is called **destructive distillation.** Certain volatile materials, such as wood alcohol and acetic acid, are evolved during this treatment. In the older processes for making charcoal these were allowed to escape, but in a modern plant (Fig. 145) they are condensed and used. **Coke** is still another common substance which is essentially amorphous carbon. It is formed from coal in exactly the same way that charcoal is made from wood. Both coke and charcoal are used as fuels and as reducing agents in metallurgical operations.

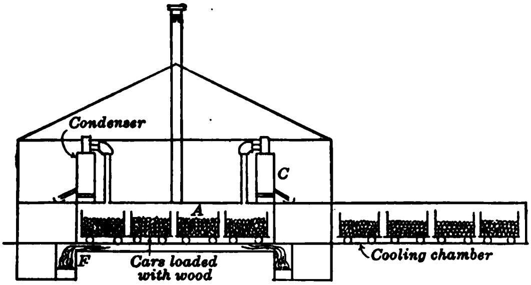


Fig. 145. Modern plant for making wood charcoal.

The reduction of copper oxide with carbon will illustrate this use. We heat a mixture of black copper oxide and charcoal in a hard-glass test tube (Fig. 146) and lead the gas evolved into limewater. The white precipitate shows carbon dioxide. Metallic copper is left in the tube:

$$2\,CuO + C \longrightarrow 2\,Cu + CO_2 \uparrow$$

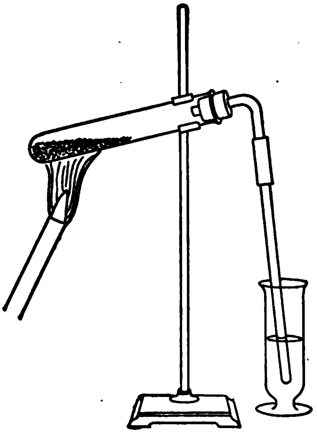


Fig. 146. Reduction of copper oxide by carbon.

We shall mention only a few of the other forms of amorphous carbon. **Lampblack** is made by burning certain oils in a limited supply of air and collecting the soot. It is almost pure carbon. Large quantities are used in the manufacture of printer's ink and paint. The charcoal which is made by heating bones without access of air is called **animal charcoal**, or **boneblack**. Thus we see that coke, charcoal, and boneblack are produced by the destructive distillation of coal, wood, and bones respectively.

248. Coal. The most important variety of amorphous carbon is coal (Fig. 147). The coal we burn to-day was once living vegetation. This has long been buried under beds of sand as the result of certain geological changes which have taken place in the earth's crust, and has been subjected to pressure and fairly high temperatures. In consequence the vegetable material has undergone a partial decomposition, yielding amorphous carbon as the main product. **Anthracite coal** (hard coal) is about 90 per cent carbon, nearly all of which is in the uncombined state. **Bituminous coal** (soft coal) contains somewhat less carbon; a considerable part of it is combined with hydrogen, oxygen, nitrogen, and sulfur. Coal is used directly as a fuel and also for the manufacture of coke.

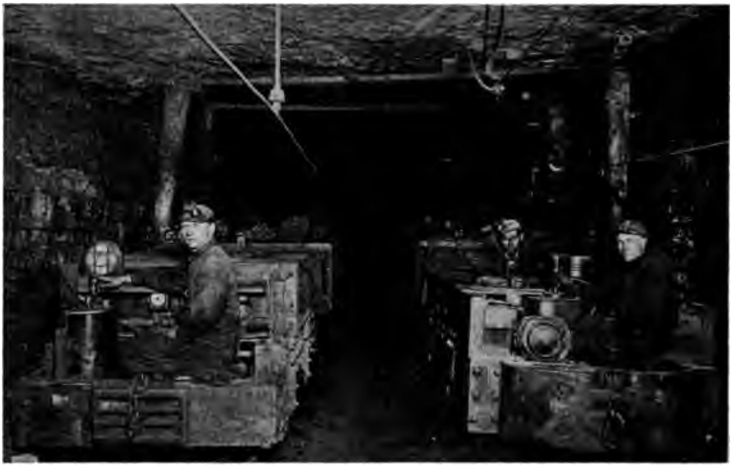


Fig. 147. Gangway in a coal mine, showing two electric locomotives hauling out trains of coal cars.

The plant for the production of coke (Fig. 148) consists essentially of the following parts: iron retorts or ovens in which the soft coal is heated; a series of towers and scrubbers through which the gases pass in order to remove heavy, tarry material (coal tar), ammonia gas, and

hydrogen sulfide; a gas holder to collect the purified coal gas. The coke is left in the retorts. Coal tar and ammonia, as well as the coal gas and the coke, are of great commercial value.

249. Chemical behavior of carbon. None of the forms of carbon react with either bases or acids. They do not dissolve in ordinary solvents, although melted iron does dissolve carbon to a certain extent. At ordinary temperatures *all forms of carbon are very inert;* but at high temperatures they all burn, forming carbon dioxide, or, in a limited supply of oxygen, carbon monoxide. At high temperatures carbon acts as a reducing agent and thus removes oxygen from the oxides of many metals. This is essentially the process of producing metals from their ores.

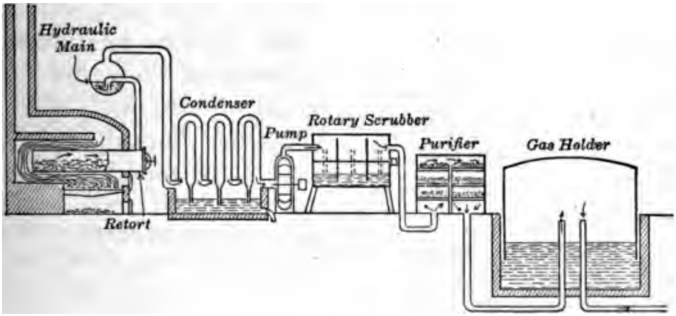


Fig. 148. Diagram of a plant for making coal gas and its by-products.

250. Coal as a fuel. Carbon in the form of coal is the source of nearly all the energy which is used to run our factories and to keep us warm in winter. But carbon alone is not sufficient; we must burn it, and in order to burn it we must have oxygen. Thus both carbon and oxygen are necessary for the production of the energy which is set free when they combine. When we buy a ton of coal we are not especially interested in the gases which go up the chimney or in the ashes left behind, but we are interested in the **energy** produced.

Heat is the form of energy with which we are most familiar. We must recall that heat, light, and electricity, are all forms of energy. The energy of anything is its **capacity for doing work.** *Energy,* like matter, *may be transformed, but it can never be created or destroyed.* This has been called the Law of Conservation of Energy. Since energy has no weight, it must be measured by some effect which it produces.

251. How we measure heat. Experiments show that if one pound of hard coal could be completely burned, and if all the heat generated in this process could be used to heat water, the temperature of one ton of water would be raised about 7° F. Engineers reckon the heat value of fuel in units, each of which *is equal to the heat required to raise the temperature of one pound of water one degree Fahrenheit.* This heat unit is called the **British thermal unit** and is written **B.t.u.** For example, the heat value of a pound of coal varies from 11,000 to 16,000 B.t.u.

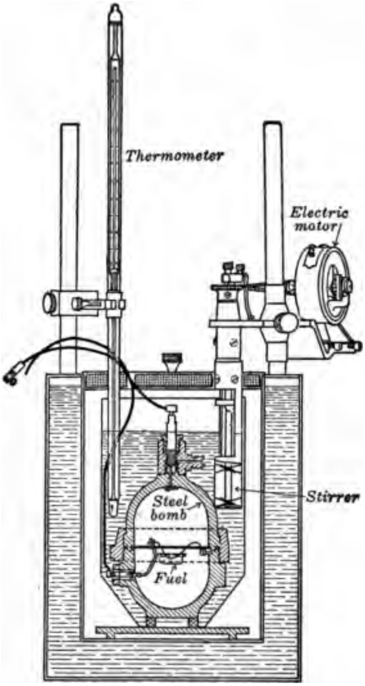


Fig. 149. Bomb calorimeter used to measure the heat value of coal.

The heat unit used in Europe and in all physical and chemical laboratories is a metric unit called the **calorie.** *A calorie is the heat required to raise the temperature of one gram of water one degree centigrade.*

252. Calorimeter. The instrument which is used to determine the heat value of a fuel is called a **calorimeter** (Fig. 149).

The apparatus consists of a strong steel cup, or bomb, with a tightly fitting screw cap. A sample of coal (about 1 g.) is weighed and placed in the little tray inside the steel cup, and a piece of platinum wire is connected to the electrodes of the bomb and allowed to dip into the coal. Then the cap is screwed into place, and oxygen is forced in under considerable pressure. The cup is now placed in a can of water which is surrounded by air space and more water, and the outside container is covered with felt. The apparatus is provided with a thermometer reading to 0.001° C. and has a mechanical stirrer. The coal is fired by sending an electric current through the platinum wire. The rise of temperature is noted. From the weight of the water and its rise in temperature (after making several corrections), the heat value of the coal can be computed.

Another type of fuel calorimeter, known as *Parr's* Peroxide Bomb, does not use oxygen gas as just described. Sodium peroxide is mixed with the fuel sample and ignited in the bomb. This apparatus is less expensive and sufficiently accurate for approximate determinations.

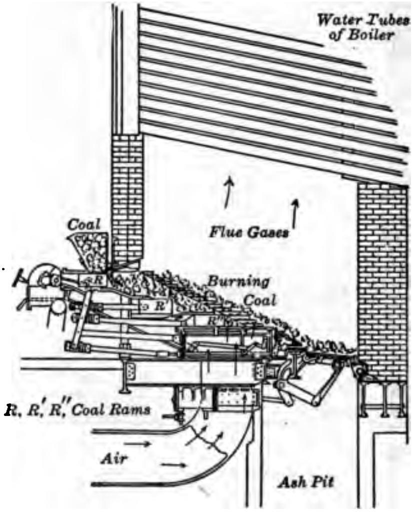


Fig. 150. Boiler with underfeed automatic stoker, which gives smokeless combustion.

253. Fuels and smoke.

Coal, coke, wood, and charcoal are common forms of **solid fuel.** When heated sufficiently these substances burn, producing carbon monoxide and carbon dioxide. This chemical reaction is called **exothermic** because *heat is liberated.* When 12 grams of carbon (its atomic weight) are burned to carbon dioxide, the amount of heat generated is 96,480 calories. Since this heat is an important result of the reaction we may express it as follows:

$$C + O_2 \longrightarrow CO_2 + 96{,}480 \text{ cal.}$$

In large furnaces much carbon monoxide and unconsumed coal in the form of fine particles may escape if insufficient air is supplied or if the furnace is not properly constructed. This unconsumed coal is responsible for the **smoke** which has become such a serious public nuisance in many of our cities where large quantities of soft coal are burned. The smoke involves in addition an enormous waste of fuel. By properly designing the fire box of the furnace (Fig. 150) and by regulating the supply of fuel and air, complete combustion will ensue, and no smoke will be formed. This is economical from the point of view of the factory, and is very desirable for those who inhabit the surrounding country.

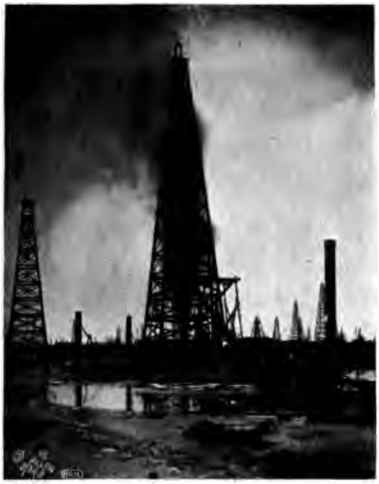


Fig. 151. Derricks of oil wells. One well gushing forth petroleum.

254. Petroleum. Petroleum is a very complex mixture of a number of compounds of carbon and hydrogen called **hydrocarbons.** It occurs in large quantities underneath the surface of the earth in many parts of the United States and in some other countries. The crude oil is pumped from wells (Fig. 151). Some of it is used directly as a fuel and is called crude burning oil. The greater portion is sent through long pipe lines (Fig. 152) to the seaboard, where it is refined. This process of refining consists in distilling the substance and then removing certain ill-smelling and tarry materials.

The distillation is carried out so that different portions which boil at different temperatures are collected separately. The low-boiling fraction (between 70° and 150° C.) is called **gasolene** and is used extensively for automobiles and gas engines. The next portion (boiling between 150° and 300° C.) is called **kerosene** and is used as a burning oil. It will not take fire directly, but if allowed to moisten a wick in a suitable lamp will burn with a pleasant, luminous flame.

Fig. 152. Pipe line for transmitting petroleum.

Certain kinds of crude petroleum yield on distillation high-boiling oils (**lubricating oils**) and a solid wax-like material, paraffin. Such oils are said to have a "paraffin base." Other varieties of petroleum do not give lubricating oils and paraffin but a thick, black pitch, which is used in roofing and paving (Fig. 153); such oils are called "asphaltic." Pennsylvania petroleum has a paraffin base, Mexican and Californian oils are for the most part asphaltic. "Liquid petrolatum," or "Russian oil," is the high-boiling distillate from still another variety of oils known as the "naphthene base" oils. Russian oil is widely used as a laxative in medicine.

Fig. 153. Applying tar to roads.

Of all the products obtained from petroleum gasolene is at present the most valuable. To increase the available supply some of the higher-boiling liquids have been decomposed into simpler molecules, which constitute the lower-boiling liquids. This process, which is called "cracking of oils," consists in vaporizing the oils and then heating the vapor (about 500° C.) under pressure (about 12 atmospheres) in an iron apparatus.

Oils derived from petroleum are used very extensively as fuel. When they burn, carbon dioxide and water are produced. They are to a small extent burned with the aid of a wick, as in the case of kerosene. For the most part they are blown out from a nozzle in the form of a fine spray mixed with air or steam. This spray is ignited and gives a very long, hot flame. Locomotives and steamships are sometimes fired with crude oil. Oil is also used as a fuel in a number of manufacturing processes.

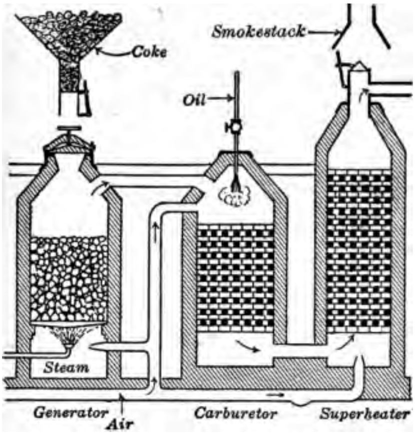


Fig. 154. Diagram of a water-gas plant.

255. Gaseous fuels. In certain parts of the United States a mixture of gases issues from the ground which is called **natural gas.** The chief constituent of this gas is methane (CH_4). Natural gas burns with a luminous flame; it is used for lighting and heating purposes in many of our cities, and as fuel in many industries. The gas obtained in the destructive distillation of coal is called **coal gas.** It also contains methane and in addition hydrogen, carbon monoxide, and some complex compounds of carbon. As it burns with a luminous flame it is used for lighting purposes in many cities. **Water gas** is a mixture of hydrogen and carbon monoxide produced by passing steam over red-hot coal. The reaction is:

$$H_2O + C \longrightarrow CO + H_2 - 26{,}990 \text{ cal.}$$

It will be noticed that in this reaction heat is absorbed; that is, heat must be supplied to keep it going. Such a reaction is called **endothermic.**

The **process of making water gas** (Fig. 154) is carried out by alternately allowing a mass of coal to burn in air until it becomes red-hot, and then shutting off the air and blowing in steam; the water gas which is formed in the second part of the process is collected. When the temperature has fallen too low the steam is shut off and air again admitted. Since hydrogen and carbon monoxide both burn with nonluminous flames water gas must be treated before it can be used for lighting purposes. This is done by adding certain volatile petroleum oils. The process is called **enriching.**

There is another gas which is used in many metallurgical operations and as a fuel for gas engines; this is called **producer gas.** It is made by forcing air through a very deep coal fire in the generator (Fig. 155). The resulting gas mixture contains all the nitrogen of the air, but all of the oxygen has combined with carbon to form carbon monoxide. Often a little steam is introduced with the air and is reduced as in the making of water gas. If made in this way producer gas is composed mainly of nitrogen, carbon monoxide, and hydrogen.

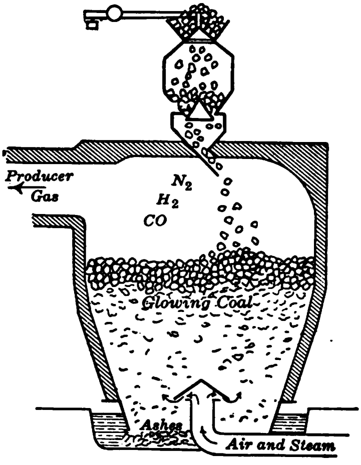


Fig. 155. **Diagram of a producer-gas plant.**

In the accompanying table the approximate composition of these various fuel gases is expressed in percentage by volume.

NAMES OF GASES	FORMULAS	PENNA. NATURAL GAS	COAL GAS	ENRICHED WATER GAS	PRODUCER GAS
Hydrogen	H_2		46	32	12
Methane	CH_4	82	34	20	3
Other hydrocarbons		17	4	17	
Carbon monoxide .	CO		8	26	21
Carbon dioxide . .	CO_2		3	3	7
Nitrogen	N_2	1	5	2	57
		100	100	100	100

256. The hydrocarbons. The natural oil, petroleum, is a mixture of hydrocarbons. There are several hundred of these compounds of carbon and hydrogen known, and they may be grouped into series according to their composition. One group is called the **paraffin series**, of which only the first six are given in the following table:

HYDROCARBONS OF THE PARAFFIN SERIES

NAME	FORMULA	MOLECULAR WEIGHT	BOILING POINT
Methane	CH_4	16	−160°C
Ethane	C_2H_6	30	−93 °
Propane	C_3H_8	44	−45 °
Butane	C_4H_{10}	58	+ °
Pentane	C_5H_{12}	72	36 °
Hexane	C_6H_{14}	86	71 °

It will be noticed that the series starts with **methane**, the principal component in natural gas, and that the difference between each two successive members in the list is CH_2. It will also be noticed that the number of hydrogen atoms is twice the number of carbon atoms plus two. This fact can be expressed in the general formula C_nH_{2n+2}. The members of this series have higher boiling points as the molecules become larger; so that the first four are gases, the next ten are liquids under ordinary conditions, and above that they are solids. Members of this series have been studied at least as far as hexacontane ($C_{60}H_{122}$).

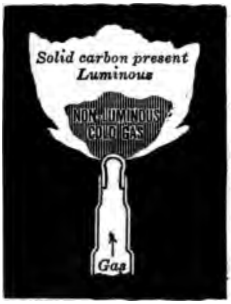


Fig. 156. Parts of a gas-jet flame.

But even this long succession of compounds does not include all the hydrocarbons. Ordinary coal gas owes its luminosity to **ethylene** (C_2H_4), which is the first member of another series with the general formula C_nH_{2n}. There is yet another group which begins with acetylene (C_2H_2) and has the general formula C_nH_{2n-2}. *All these hydrocarbons are mutually soluble* so that mixtures can be made in any proportion.

257. Gas burners and flames. When gas burns in the ordinary **fishtail burner**, it is spread out in a thin sheet by the tip so that sufficient air is brought into contact with the gas to burn all of the carbon. In the flame itself some of the complex carbon compounds are broken down into free carbon by the high temperature. This free carbon is heated white-hot by the combustion which is going on, and it is these particles of incandescent carbon which give the flame its illuminating power. Water gas contains no such carbon compounds and must therefore be enriched. Figure 156 shows the structure of this type of flame. It will be noticed that there are several distinct zones. The luminous zone is full of particles of white-hot carbon, which on passing to the outer zone are completely consumed, forming carbon dioxide; the heat given off in this combustion keeps the flame at the necessary temperature.

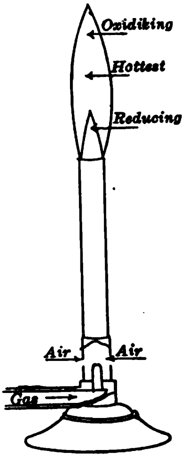


Fig. 157. Bunsen burner and flame.

In a **Bunsen burner** (Fig. 157) we admit air into the interior of the flame. This cools down the flame so much that the temperature is not high enough to decompose the complex carbon compounds into free carbon; the flame is therefore nonluminous. The burners on a gas range (Fig. 158) are modified Bunsen burners, so arranged as to give a large number of small blue flames.

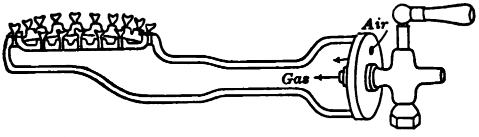


Fig. 158. Burner used on a gas range.

In a **Welsbach lamp** we have a mantle which is made incandescent by the heat of a Bunsen flame (Fig. 159). When such mantles are used it is not necessary to enrich the gas with illuminants. The Welsbach mantles are composed of the oxides of two rare elements, thorium and cerium. By their use with the same amount of gas the consumer gets *four times as much light* as with an ordinary burner.

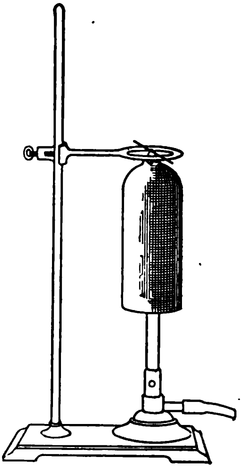


Fig. 159. Welsbach mantle and Bunsen burner.

258. Uses of acetylene. Acetylene (C_2H_2) is a gas which is produced by the action of water on calcium carbide:

$$CaC_2 + 2\,H_2O \longrightarrow Ca(OH)_2 + C_2H_2$$

It can either be generated as required, or can be conveniently dissolved in a liquid known as acetone in a tank under pressure. Acetylene will burn with a very luminous flame in an especially constructed burner (Fig. 160) which admits air. It is used to a limited extent for illuminating purposes. If oxygen is blown through such a flame complete combustion of the acetylene takes place and we obtain a very hot nonluminous flame. This flame is one of the hottest known and is used extensively because it will easily melt iron and other metals.

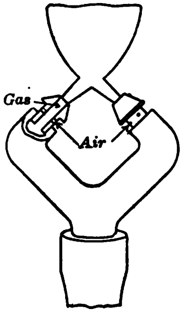


Fig. 160. Acetylene-burner tip.

Acetylene is an endothermic compound, and when it decomposes heat is generated, as shown in the following equation:

$$C_2H_2 \longrightarrow 2\,C + H_2 + 49{,}300 \text{ cal.}$$

In the acetylene flame the heat of combustion of the carbon and hydrogen is added to this heat of decomposition:

$$2\,C_2H_2 + 5\,O_2 \longrightarrow 4\,CO_2 + 2\,H_2O + 603{,}000 \text{ cal.}$$

With the right mixture of oxygen and acetylene it is possible to get a temperature of about 2700° C. The **oxyacetylene torch**, which is very much like the oxyhydrogen blowpipe, cuts steel by melting it (Fig. 161). The tip of the flame when drawn slowly over the metal melts it at the point of contact and so cuts the metal into pieces. It is especially useful in dismantling steel structures.

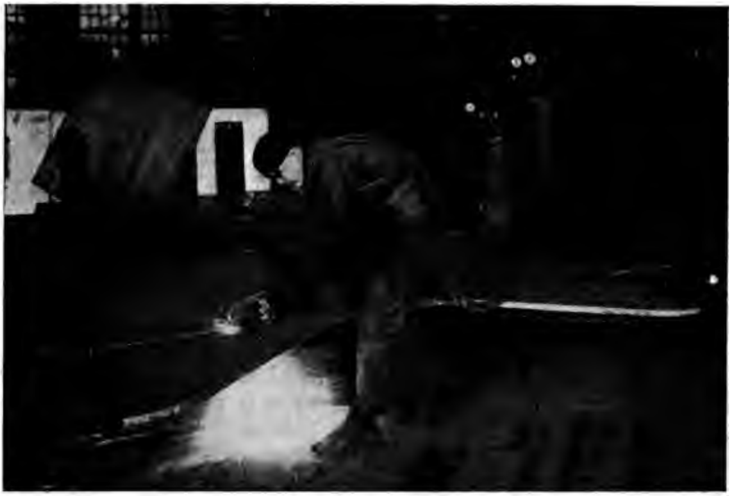


Fig. 161. Cutting steel with an oxyacetylene torch.

Pieces of iron and other metals may be joined together by heating them until they melt and then allowing the molten metal to fuse together. This process is called **oxyacetylene welding**, and is of great importance in the industries. Its most general application is in welding thin metal, such as the parts of steel railway cars, repairs on railway rolling stock, and the cutting up of large masses of steel, as the wrecked frames of buildings, bridges, and the like. Strength tests on welds show that a weld is about 85 per cent as strong as the same thickness of plate.

SUMMARY OF CHAPTER XXII

CARBON FORMS AN ENORMOUS NUMBER OF COMPOUNDS, especially with hydrogen, oxygen, and nitrogen.

THE THREE ALLOTROPIC FORMS of carbon are *diamond, graphite,* and *amorphous carbon.* They have different physical properties, but all yield carbon dioxide when burned in sufficient oxygen.

CARBON IS INERT at ordinary temperatures but burns at high temperatures. It is a reducing agent. It reacts with lime to form calcium carbide when heated in an electric furnace.

USES OF CARBON in different forms are —

Diamond: gem and abrasive;
Graphite: lead pencils, lubricant, crucibles, and electrodes;
Coal: fuel and in manufacture of illuminating gas and coke;
Coke: ore reducer, fuel, and in making water gas;
Lampblack: printer's ink and paint;
Boneblack: decolorizing sugar and oils.

MOST IMPORTANT FUEL IS COAL. Heat is measured in *calories.* A calorie is the heat required to raise one gram of water one degree centigrade. Engineers' heat unit is B. t. u. (British thermal unit).

CHEMICAL REACTIONS which give out heat are called *exothermic;* a few reactions absorb heat and are called *endothermic.*

FUELS are substances which burn in air. The reaction is strongly exothermic; we carry out this reaction because we want the heat evolved.

SOLID FUELS are coal, coke, wood, and charcoal.

PETROLEUM is a *mixture of hydrocarbons.* Gasolene, kerosene, and crude fuel oil are obtained from petroleum.

FUEL GASES include natural gas, coal gas, water gas, and producer gas. Fuel gases which contain hydrocarbons burn with a luminous flame because carbon is set free.

ACETYLENE is produced from calcium carbide. The oxyacetylene flame is extremely hot and is used for cutting and welding metals.

QUESTIONS AND PROBLEMS

1. What is the easiest way to show the presence of carbon in a compound?

2. What is the most useful form of carbon? Explain. What is the most expensive form? Why?

3. What are the by-products in the coal-gas industry?

4. How do we measure the fuel value of coal?

5. What are characteristics of a good fuel?

6. Why is crude oil such an excellent fuel for locomotives and steamships?

7. How would you prove that carbon dioxide and water are formed when kerosene burns?

8. Why is it desirable to remove the sulfur compounds from illuminating gas?

9. Why is producer gas not used for illuminating purposes?

10. Which fuel gas is richest in hydrogen? in methane? in carbon monoxide? (Examine table.)

11. Why is not the flame used in a gas range smoky?

12. Why are Welsbach mantles not more generally used?

13. For what especial purposes is the acetylene lamp adapted?

14. How many tons of oxygen are required to burn completely one ton of coal which is 90% carbon?

15. How many tons of carbon dioxide are produced in Problem 14?

16. How many grams of carbon will be required to reduce 10 g. of copper oxide to metallic copper?

17. Write the equation for the complete combustion of acetylene.

18. How many liters of air are required to burn 1 liter of acetylene?

TOPICS FOR FURTHER STUDY

Fuels. If possible, see in operation furnaces or stoves burning gas, oil, and coal mechanically stoked. What are some of the relative merits of each fuel? In certain parts of the country only anthracite coal is used in the homes; why? The iron blast furnace requires anthracite coal or coke as a fuel; the glass industry requires gas or oil. Explain. (*Cressy's* Discoveries and Inventions, *Bird's* Modern Science Reader, and *Findlay's* Chemistry in the Service of Mankind.)

CHAPTER XXIII

THE SIMPLER COMPOUNDS OF CARBON

Organic compounds — alcohol, preparation and properties — alcoholic liquors — industrial alcohol — empirical and structural formulas — other alcohols — ether — carbon tetrachloride and chloroform — aldehydes — acids — esters — fats — soap — other hydrocarbons — coal-tar products and dyes.

259. Organic and inorganic compounds. The most striking characteristic of carbon is its ability to form almost numberless compounds in which a whole series of carbon atoms are linked to one another. These are called **organic compounds**; compounds of all the other elements are called **inorganic compounds.** We can define *organic chemistry as that branch of chemistry which deals with the compounds of carbon.* The elements which often appear with carbon are hydrogen, oxygen, nitrogen, the halogens, and sulfur; a few other elements sometimes are constituents of organic compounds, but they are of minor *importance.* There are over 100,000 known organic com-

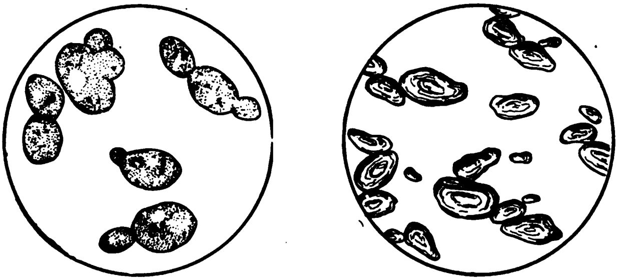


Fig. 162. Yeast cells as seen under a microscope.

pounds; in this chapter we shall consider some of the simpler and more important of these.

260. Ordinary alcohol (C_2H_5OH). This compound is the product obtained from the fermentation of sugars, a chemical process brought about by the presence of small living plants, of which yeast (Fig. 162) is a common example. The other product of the fermentation is carbon dioxide:

$$\underset{\text{sugar}}{C_6H_{12}O_6} \longrightarrow 2\ \underset{\text{alcohol}}{C_2H_5OH} + 2\ \underset{\substack{\text{carbon}\\\text{dioxide}}}{CO_2\uparrow}$$

Alcohol may be prepared in the laboratory by making a 10 per cent solution of sugar or molasses in water, pouring it into the flask shown in figure 163, and then adding a little yeast which has already been dissolved. If this is kept for a day at about 30° C. the bubbles of carbon dioxide will rise to the surface and can be led off through limewater, as shown in the figure. To prevent the carbon dioxide of the air from affecting the limewater, we may attach a tube of sodium hydroxide sticks. The alcohol is separated from the solution by distillation.

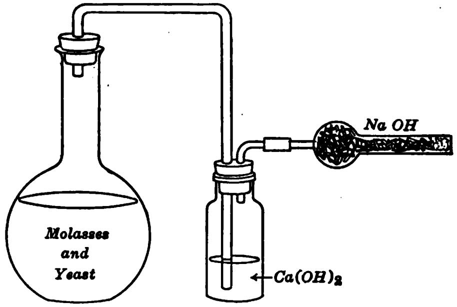


Fig. 163. Preparation of alcohol in the laboratory.

When a mixture of alcohol and water is distilled, the liquid begins to boil at about 78° C., which is the boiling point of pure alcohol. As the process continues the boiling point rises until it reaches 100° C., the boiling point of water. If the distillate (what is distilled over) is separated into **fractions** according to the temperature, the first fraction collected contains a large percentage of alcohol, while the fractions collected during the latter part of the process will be mainly water. On a large scale the distillation is carried out in an apparatus having a tall **fractionating column** (Fig. 164) and partial condenser. The water vapor is condensed in the fractionating column and partial condenser and returns to the still; the more volatile alcohol passes on until it reaches the total condenser. The distillate is 95 per cent alcohol, and the liquid returning to the still is largely water. This process is called **fractional distillation** and is very similar to that used in the distillation of petroleum.

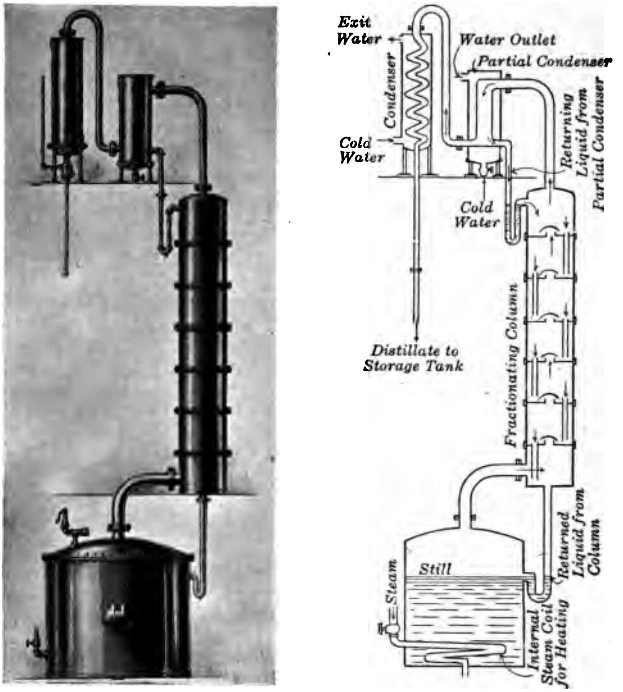

Exit Water
Water Outlet
Partial Condenser
Condenser
Cold Water
Returning Liquid from Partial Condenser
Cold Water
Fractionating Column
Distillate to Storage Tank
Still
Steam
Internal Steam Coil for Heating
Returned Liquid from Column

Fig. 164. Commercial still with fractionating column.

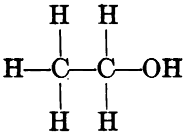
261. Properties and uses of alcohol. Pure alcohol is a colorless liquid boiling at 78° C.; it is inflammable and is used to some extent as a fuel. It is an excellent solvent, dissolving many substances which are only slightly soluble in water. It is the solvent used in making varnishes for wood and lacquers for metal, as well as in the manufacture of celluloid, collodion, and artificial silk. It mixes with water in all proportions but is not ionized in aqueous solution; it does not interact with dilute acids, bases, or salts.

Commercially alcohol is made from the starch of potatoes or grains, such as corn. It is commonly known simply as alcohol, but the chemist calls it **ethyl alcohol** to distinguish it from other alcohols, such as methyl, or wood alcohol.

262. Alcoholic Liquors. Alcoholic beverages are prepared by allowing different substances to ferment. Wine contains from 8 to 15 per cent of alcohol and is formed by the fermentation of grape juice. Beer contains only about 5 per cent of alcohol and is prepared by allowing a mixture of grains and water to ferment under special conditions. **Distilled liquors** are made by the fractional distillation of fermented liquors like wine or beer. Brandy is distilled wine; whisky and gin are essentially distilled beers; they all contain from about 40 to 50 per cent of alcohol. Since January 16, 1920 the use of alcoholic beverages has been prohibited in the United States, and pure alcohol can be purchased only for certain special purposes under strict regulations.

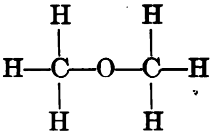
263. Industrial alcohol. The price of ordinary alcohol is about $7.20 per gallon, of which $6.60 is the tax imposed by the government. Since the high price prevented the extensive industrial use of alcohol, Congress in 1907 passed an act enabling dealers to sell alcohol which contained certain poisonous substances without the tax. These poisonous substances, which make impossible the use of this alcohol as a beverage, are ordinarily wood alcohol and benzene (C_6H_6). The mixture is called **denatured alcohol**; it is suitable for varnish making and other industrial operations.

264. Formula of ethyl alcohol. The formula of ethyl alcohol might be written C_2H_6O, which tells us that there are 2 carbon atoms, 6 hydrogen atoms, and 1 oxygen atom. This is called **an empirical formula** and states the facts derived from the percentage composition and molecular weight of the substance. It would be sufficient for most of the inorganic compounds which we have thus far studied. But it is inadequate in organic chemistry, for *it often happens that there are several compounds which have the same empirical formula.* For example, there is another substance, called methyl ether, which also has the formula C_2H_6O but which is a gas having totally different properties from ethyl alcohol. The difference between these two substances must lie in the way their atoms are joined together. We are thus led to inquire how the atoms are linked and to show this linkage in our formulas. Accordingly we write them graphically as follows:



$$\begin{array}{ccccccc} & & H & & H & & \\ & & | & & | & & \\ H & — & C & — & C & — & OH \\ & & | & & | & & \\ & & H & & H & & \end{array}$$

ethyl alcohol



$$\begin{array}{ccccccccc} & & H & & & & H & & \\ & & | & & & & | & & \\ H & — & C & — & O & — & C & — & H \\ & & | & & & & | & & \\ & & H & & & & H & & \end{array}$$

methyl ether

Since these formulas show how every atom in the molecule is joined to every other one, they are called **structural** formulas. We usually condense such a formula as that of alcohol and write it C_2H_5OH.

We cannot here consider how these structural formulas are derived; it is enough to say that they rest on a mass of experimental evidence. They tell the trained chemist how a given substance will probably react, because he knows that certain linkages represent certain reactions. It has been found that in organic compounds carbon always has the valence 4, and this point is useful in remembering and writing structural formulas. Although a formula means very little in organic chemistry unless it is of the structural type, nevertheless we shall sometimes use the empirical formula when the structural formula is very complicated.

265. Other alcohols. Another well-known substance is ***wood alcohol***, or **methyl alcohol**, which has the formula CH_3OH.

It is prepared, as we have seen, in the destructive distillation of wood. It resembles ethyl alcohol in many of its properties and is used as a solvent and as an agent for denaturing ethyl alcohol *since it is very poisonous.*

There are besides these two a great many other substances called alcohols. They all react in such a way that we represent them by a formula in which a hydroxyl group (OH) is attached to a carbon atom. The following table shows the names and formulas of a number of alcohols and of the corresponding hydrocarbons of the methane series:

CH_4 (methane)	CH_3OH (methyl alcohol)
C_2H_6 (ethane)	C_2H_5OH (ethyl alcohol)
C_3H_8 (propane)	C_3H_7OH (propyl alcohol)

We may regard an alcohol as being derived from the hydrocarbons by substituting for one or more hydrogen atoms a corresponding number of hydroxyl groups. It should be noted that this is a method of showing relationship on paper and does *not* represent a reaction which we carry out in the laboratory. Accordingly, in the series it will be noticed that each alcohol differs from the one above in that it contains one more atom of carbon and two more atoms of hydrogen (CH_2). Such a series of organic compounds which differ from one another by a constant number of carbon and hydrogen atoms is called an **homologous series.** All members of such a series have very much the same chemical properties, but their physical properties gradually differ as we go up the series. There are a great number of homologous series in the different classes of organic compounds.

266. Ether. When alcohol is treated with sulfuric acid under certain conditions, **ethyl ether** and water are formed. Ethyl ether has the structure represented by the formula $(C_2H_5)_2O$ and may be regarded as ethyl oxide. The equation for its formation is

$$\underset{\text{ethyl alcohol}}{2\,C_2H_5OH} \longrightarrow \underset{\text{ethyl ether}}{(C_2H_5)_2O} + H_2O$$

It will be noticed that in ether we have two groups of carbon and hydrogen atoms (C_2H_5) joined together by an oxygen atom. This is a characteristic linkage of a whole homologous series which are known as **ethers.** The lowest member of this series is **methyl ether** (CH_3OCH_3), of which we have already spoken. By comparing its formula with that of alcohol we can see that the substances are entirely different although they contain the same number of carbon, hydrogen, and oxygen atoms. Substances which have the same empirical formulas but different structural formulas are called **isomers.** The number of isomers in organic chemistry is very large, and it is because of this fact that only structural formulas have any real meaning in that subject.

Ethyl ether, or, as it is usually called, simply ether, is a colorless liquid boiling at 35° C. It is prepared on a large scale and is used extensively as a solvent and as an anæsthetic. It produces unconsciousness when inhaled and has been used for a number of years in surgical operations.

267. Carbon tetrachloride and chloroform. Substances which are derived from hydrocarbons by the exchange of one or more hydrogen atoms for a corresponding number of atoms of some other element, or for an equivalent number of radicals, are called **substitution products.** Chlorine forms several substitution products of methane. If we replace all four hydrogen atoms in methane with chlorine, we obtain a compound called **carbon tetrachloride** (CCl_4). As a matter of fact, the reaction between chlorine and methane is very hard to control, and pure methane is not easy to obtain; therefore carbon tetrachloride is actually prepared by another reaction. Carbon disulfide (CS_2) readily reacts with chlorine, forming sulfur chloride and carbon tetrachloride; the two liquids can be separated by distillation:

$$\underset{\substack{\text{carbon}\\\text{disulfide}}}{CS_2} + \underset{\text{chlorine}}{3\,Cl_2} \longrightarrow \underset{\substack{\text{sulfur}\\\text{chloride}}}{S_2Cl_2} + \underset{\substack{\text{carbon}\\\text{tetrachloride}}}{CCl_4}$$

Carbon tetrachloride is a heavy, colorless liquid boiling at 79° C. and has an odor not unlike that of chloroform. It readily dissolves greases, gums, and resins. As a noncombustible solvent it finds a wide use in technical operations. When mixed with gasolene it is sold as a cleansing fluid under various trade names, such as "Carbona." It is the main part of the fluid used in certain small fire extinguishers (Fig. 165). When squirted on the fire it forms a very heavy vapor, which hangs over the burning material, excluding the air and thus extinguishing the flames. It is particularly valuable in putting out burning oil since such fires cannot be extinguished by water; for oil simply floats on the water and continues to burn.

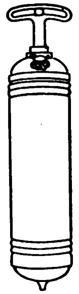


Fig. 165. "Pyrene" fire extinguisher.

Carbon tetrachloride can be reduced to a substance called **chloroform** ($CHCl_3$):

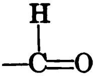
$$\underset{\text{carbon tetrachloride}}{CCl_4} + \underset{\text{nascent hydrogen}}{2[H]} \longrightarrow \underset{\text{chloroform}}{CHCl_3} + \underset{\text{hydrogen chloride}}{HCl}$$

Chloroform can also be prepared by the action of bleaching powder on ethyl alcohol. It is a sweet-smelling, volatile liquid, which finds certain uses as a solvent and as an anæsthetic. It is not so safe an anæsthetic as ether and is employed only in special cases.

268. Aldehydes. Methyl alcohol can be oxidized to form a substance called formaldehyde (HCHO):

$$\underset{\text{methyl alcohol}}{CH_3OH} + [O] \longrightarrow \underset{\text{formaldehyde}}{HCHO} + H_2O$$

If we write out this formula in full we see that the oxygen atom has two bonds linking it to the carbon atom. The group



$$\overset{H}{\overset{|}{—C=O}}$$

is the characteristic of a whole class of compounds known as **aldehydes.**

269. Formaldehyde is a gas with a penetrating odor, which causes the eyes to smart. It is used in water solution as a disinfectant and an antiseptic. The 40 per cent solution is sold under the name **formalin.** A solid compound called paraformaldehyde, when heated, breaks down to give the gas. This substance is often sold as a candle (Fig. 166), which can be lighted in a room for disinfection.

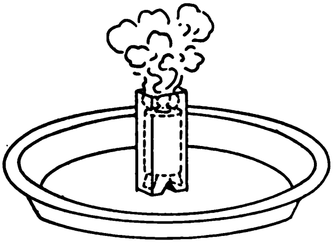
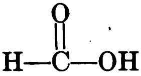


Fig. 166. Formaldehyde candle.

270. Acids. Formaldehyde can be further oxidized to a liquid called **formic acid** (HCOOH). The structural formula shows a doubly linked oxygen atom connected with the carbon atom, and also a hydroxyl group; thus:



$$H-\overset{\overset{O}{\|}}{C}-OH$$

formic acid

This combination (COOH) is called the **carboxyl group** and is characteristic of a class of organic substances known as **acids.** They are obtained by oxidizing the corresponding alcohols. There are a number of series of acids; formic acid is the lowest member of a series called the fatty acids, the lower members of which are liquids and the higher members solids. They are all monobasic and form salts on neutralization. Formic acid is a fairly strong acid, but the acids become progressively weaker as the number of carbon atoms increase. Two of the higher acids which are solids, palmitic ($C_{15}H_{31}COOH$) and stearic ($C_{17}H_{35}COOH$), are derived from fats, hence the name of the series.

Acetic acid (CH_3COOH) is the most important lower member of this series. It can be prepared in the laboratory by oxidizing ethyl alcohol, but it is actually obtained as a by-product in the distillation of wood. Vinegar is essentially a dilute solution of acetic acid obtained by the oxidation of dilute alcohol by bacteria. Since it is a rather weak acid it is used in the industries when a weak acid is desired.

Among the other well-known organic acids are **tartaric acid**, which occurs in many fruits such as grapes, and **citric acid**, which is contained in fruits like oranges and lemons. The ordinary household **cream of tartar**, a white solid used in baking powders, is the acid potassium salt made from tartaric acid. **Oxalic acid** is used to remove iron rust and ink from white cloth, to clean certain metals, such as copper, and to bleach straw hats; it is poisonous.

271. Esters. Alcohols and organic acids react to form water and a substance called an **ester**. For example, ethyl alcohol and acetic acid form an ester called ethyl acetate:

$$\underset{\text{ethyl alcohol}}{C_2H_5OH} + \underset{\text{acetic acid}}{CH_3COOH} \rightleftharpoons \underset{\text{ethyl acetate}}{CH_3COOC_2H_5} + H_2O$$

The reaction is reversible and usually proceeds to a point where about 80 per cent of the material is converted into the ester.

Ethyl acetate has a pleasant, fruity odor. Many esters occur naturally in fruits and flowers and are frequently the cause of their taste and smell. They may be prepared artificially for flavoring beverages and foods and for making perfumes.

Esters react with water, as indicated in the reversible reaction just given. This process, called **hydrolysis**, goes on very slowly at ordinary temperatures. They are also decomposed by strong bases, such as sodium and potassium hydroxide, with the production of alcohols and salts of the organic acids; thus:

$$\underset{\text{ethyl acetate}}{CH_3COOC_2H_5} + NaOH \longrightarrow \underset{\text{sodium acetate}}{CH_3COONa} + \underset{\text{ethyl alcohol}}{C_2H_5OH}$$

This process is called **saponification**.

272. Fats. The most important esters are those which occur naturally and are known as fats and oils. The solid animal fats are esters of palmitic and stearic acids and an alcohol called glycerin ($C_3H_5(OH)_3$), which contains three hydroxyl groups. These animal fats are really *mixtures* of the esters just described. When they are heated with water in the presence of certain catalysts, they break down almost completely into free glycerin and the free acid. The glycerin is used for a number of purposes, including the manufacture of dynamite. The solid, fatty acids are used mainly for making candles and waxes.

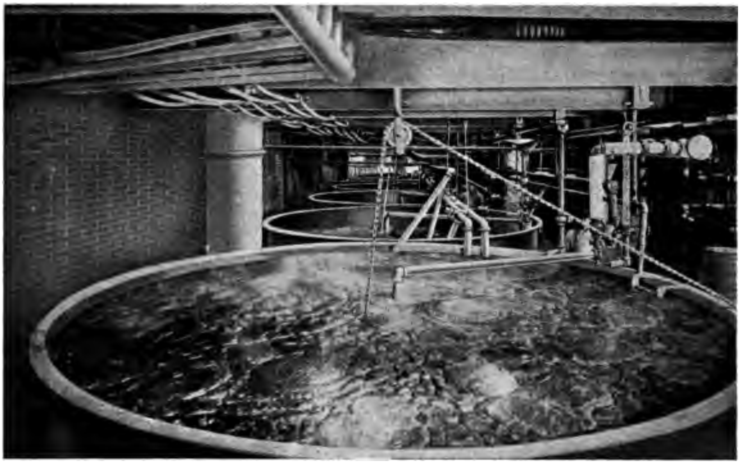


Fig. 167. Kettle used in making soap.
It contains enough stock to make 10 or 12 carloads of soap.

273. Soap. If in place of water we use sodium hydroxide we obtain glycerin and the sodium salt of the acid, which is **soap.** The following equation represents such a reaction:

$$\underset{\text{glyceryl stearate}}{\overset{\text{Fat}}{(C_{17}H_{35}COO)_3C_3H_5}} + \overset{\text{Alkali}}{3\,NaOH} \longrightarrow \underset{\text{sodium stearate}}{\overset{\text{Soap}}{3\,C_{17}H_{35}COONa}} + \overset{\text{Glycerin}}{C_3H_5(OH)_3}$$

It is not expected that the above equation will be memorized, but it is given in order to show that the reaction for making soap is similar to that for making sodium acetate. Hence the appropriateness of the name, saponification. The sodium salts are only moderately soluble in water and can be separated from the reaction mixture by the addition of common salt. In making soft soap, potassium hydroxide is used instead of *sodium hydroxide.*

In the commercial manufacture of soap the fat and the alkali are heated together in huge kettles (Fig. 167) for several days. The soap is *salted out* and rises to the top of the liquid. The glycerin, which is the other product of the reaction, is separated by distillation from the liquid containing the *spent lye*. A great variety of soaps can be manufactured, according to the nature of the fat which is used and the way in which the process is carried out.

274. Cleansing power of soap. The following seems to be the explanation of the cleansing power of soap and soap solutions. Soap is a mixture of the sodium salts of very weak acids. Consequently when it is dissolved in water the salts are almost completely hydrolyzed into free fatty acids and sodium hydroxide. These free fatty acids do not, however, precipitate out but stay in colloidal solution, probably because they combine with some of the undissociated soap. A solution of soap is therefore essentially an alkaline colloidal solution, and its cleansing action is connected with this fact. It is a more or less general property of colloidal solutions that the colloid tends to bring other substances into colloidal solution and to prevent the precipitation of substances from colloidal solution. This is called the *mutual protection of colloids*. When oil is shaken with soap solution the oil remains in the solution permanently suspended in what is essentially a colloidal solution. In the same way particles of dirt are brought into colloidal solution by soap water.

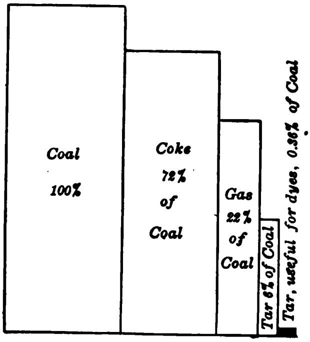
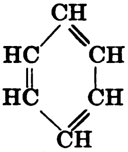


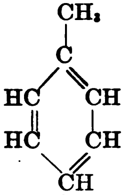
Fig. 168. Diagram to show amounts of by-products obtained in the distillation of coal.

275. Other hydrocarbons. We saw in the last chapter that there are several series of hydrocarbons which contain less hydrogen than the paraffin hydrocarbons; as, for example, the ethylene ($CH_2{=}CH_2$) and the acetylene

($CH\equiv CH$) series. In these substances the carbon atoms are joined with a **double** or **triple** bond. There is still another series of hydrocarbons called **aromatic compounds**, which are obtained as a by-product from the tar in the distillation of coal (Fig. 168). In these compounds the carbon atoms are joined together in a ring containing double bonds. The most important are **benzene** (C_6H_6), **toluene** ($C_6H_5CH_3$), and **naphthalene** ($C_{10}H_8$). All these are the starting points in the manufacture of the so-called coal-tar dyes, of many important drugs, and of certain explosives. Naphthalene itself is used directly as moth balls.

The structural formulas of benzene and toluene are as follows:


benzene


toluene

276. Carbolic acid. The hydrogen atoms of benzene and of toluene may be replaced by other atoms and groups. **Carbolic acid**, or, as it is also called, **phenol**, is a hydroxyl derivative of benzene and has the formula C_6H_5OH. Carbolic acid is another substance obtained from coal tar. It is an excellent disinfectant and is used extensively for that purpose. Strong solutions of it have a corrosive action on the flesh, and it must therefore be used with caution. A substance called **Bakelite**, somewhat resembling hard rubber, is made by the interaction of formaldehyde and phenol. It is used in the manufacture of such articles as phonograph records and for insulation in electrical machinery.

A substance closely allied to phenol is **pyrogallic acid** ($C_6H_3(OH)_3$), a reducing agent which is used as "pyro" developer in photography. Its alkaline solution absorbs oxygen from the air and so is used to determine oxygen in gas analysis.

277. Dyes. Dyes are colored compounds which can be fixed on fabrics so that they cannot easily be washed off. In the past most dyes were obtained from certain plants and trees. In the last sixty years an industry has grown up which now manufactures many of these same dyes by starting with coal tar. A host of new colors have also been developed and put on the market at a very reasonable price. These dye-stuffs are much too complicated to be considered in this book. They are all organic compounds and are made by starting with benzene, toluene, or naphthalene and preparing carefully step by step a whole series of compounds, until finally one is formed which is the required dye. Each step in a new process requires long and painstaking work in the laboratory before the best way of carrying out the preparation is discovered. It is then performed on a large scale with large apparatus. Hence, while it is true that the manufactured dye-stuffs require coal tar as the starting point, it must not be thought that the colors are already present in the tar and need only be extracted by some simple process. The same is true of a number of drugs which are sometimes called "coal-tar products."

SUMMARY OF CHAPTER XXIII

ORGANIC CHEMISTRY is the study of the compounds of carbon.

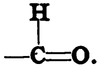
A STRUCTURAL FORMULA represents the arrangement of the atoms composing a molecule. Several compounds may have the same empirical formula. These are *isomers*.

A HYDROCARBON is composed of carbon and hydrogen only. The *methane series* has the general formula C_nH_{2n+2}; the *ethylene series*, C_nH_{2n}; the *acetylene series*, C_nH_{2n-2}; the *benzene series*, C_nH_{2n-6}.

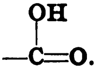
SUBSTITUTION PRODUCTS are those in which one or more hydrogen atoms of a hydrocarbon are replaced by some other element or radical. Carbon tetrachloride and chloroform are such products.

ALCOHOLS may be thought of as being derived from hydrocarbons by the substitution of one or more hydroxyl groups for a corresponding number of hydrogen atoms. *Ethyl* alcohol is made by the fermentation of sugar. *Methyl* alcohol is a by-product of the distillation of wood. *Denatured* alcohol is ethyl alcohol to which some poison has been added.

ETHER is ethyl oxide. It is prepared by the action of sulfuric acid on alcohol.



ALDEHYDES contain the group $-\overset{\substack{H\\|}}{C}=O$. Formaldehyde, the commonest aldehyde, is made by oxidizing methyl alcohol.



ORGANIC ACIDS contain the carboxyl group $-\overset{\substack{OH\\|}}{C}=O$. They can be made by oxidizing aldehydes. Formic acid, acetic acid, oxalic acid, tartaric acid, and citric acid are familiar organic acids.

ESTERS are compounds obtained by the interaction of acids and alcohols. The reaction is reversible.

FATS are glycerin esters of palmitic and stearic acid. These fats can be hydrolyzed to glycerin and the free fatty acid, both of which are useful.

SOAPS are sodium salts of the higher fatty acids. They are formed by the action of sodium hydroxide on fats.

SOAP SOLUTION is essentially a colloidal solution of a fatty acid. It cleans because as a colloidal solution it tends to take other substances, like oil and dirt, into colloidal solution and thus remove them.

BENZENE, TOLUENE, AND NAPHTHALENE are three hydrocarbons found in coal tar. In them the carbon atoms are joined in a *ring*. They are called aromatic hydrocarbons. They are the starting point for the manufacture of so-called coal-tar dyes, and many drugs and explosives.

CARBOLIC ACID, OR PHENOL, is a hydroxyl derivative of benzene, also found in coal tar. It is used as an antiseptic and in making Bakelite.

QUESTIONS

1. Why are structural formulas so much used in organic chemistry?
2. What is the relation between carbon tetrachloride and methane?

3. What is the principal source of the paraffin series of hydrocarbons?

4. Why is it not economical to make grains into alcohol?

5. Why is glycerin considered an alcohol?

6. What group of elements is characteristic of organic acids?

7. What is the relation between ethyl alcohol and acetic acid?

8. Why in organic chemistry are esters sometimes compared with salts?

9. Name three organic acids which are found in nature.

10. To what class of substances does glycerin belong?

11. What is the difference between benzene and benzine?

12. Why is alcohol sometimes mixed with water to form a non-freezing mixture for the radiator of an automobile?

13. What valuable by-product is obtained in the manufacture of soap?

14. What two explosives are made from coal tar?

15. What is the difference between a synthetic dye and a natural dye?

16. What is the catalyst used in fermentation?

17. Name five organic substances found in the home and describe how each was made.

TOPICS FOR FURTHER STUDY

Industrial alcohol. How is industrial alcohol made? What laws govern its manufacture and sale? Why? In what way is the production of cheap alcohol of benefit to many industries? (*Duncan's* Chemistry of Commerce and *Martin's* Modern Chemistry.)

The importance of coal tar. What familiar materials are derived wholly or in part from coal tar? Why is coal tar often called a by-product? How is it refined? What are coal-tar "crudes," and why are they of vital importance in time of war? Why should the textile industries be interested in coal tar and its products? (*Slosson's* Creative Chemistry, *Martin's* Modern Chemistry, and *Findlay's* Chemistry in the Service of Mankind.)

CHAPTER XXIV

LIFE AND ORGANIC COMPOUNDS

The carbohydrates: sugar, glucose, starch, cellulose — fabrics and paper — nitrocellulose.

Fats and oils — drying oils — edible oils — hydrogenation of oils.

Foods — kinds and uses — food values and composition — necessary quantity — accessory factors.

278. Carbon compounds and living matter. It was originally thought that in some peculiar way organic compounds were different from inorganic compounds. Before the middle of the last century all organic compounds had been obtained directly or indirectly from living matter, and it was believed that a " vital force " was essential for their production. This view was shattered by the synthesis of several simple organic compounds from inorganic material. Since then a great many complicated organic substances of all classes have been synthesized from such purely inorganic matter as coal, calcium oxide, and water. We now know that there *is no essential difference between organic and inorganic compounds.*

In this chapter we shall consider a few of the rather complex substances which are the principal products of animal and plant life. These compounds are put to a number of uses and are essential foods for man and beast. We shall not be able to do more than outline the process of formation of these compounds in plants and animals and shall only touch on their transformation during the life process. The branch of chemistry which deals with these matters is every day becoming more important but is obviously too complicated to be *considered here.* It is called **biological chemistry.**

The Carbohydrates

279. Composition. Sugar, starch, cotton fiber, and wood fiber are all common substances of great importance. These materials and a great many others which are products of plant life belong to a class of carbon compounds called **carbohydrates.** The carbohydrates all contain carbon, hydrogen, and oxygen. The last two elements are always present in the same proportion as in water; hence one might imagine from the empirical formula that the substance were composed of carbon and a certain amount of water. This, of course, is not the structure of the compounds, but it has given rise to the name carbohydrates. We shall consider a few important carbohydrates.

Fig. 169. Sugar beet as grown in California.

280. Ordinary sugar ($C_{12}H_{22}O_{11}$). The substance commonly called **sugar** is obtained mainly from the sugar cane and the sugar beet (Fig. 169), although it also occurs in the sugar maple and in honey.

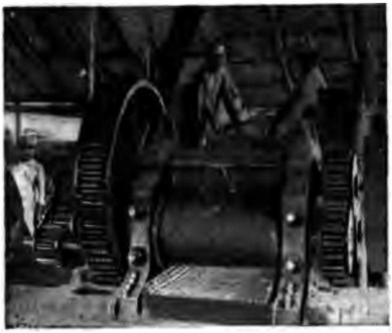


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Fig. 170. Sugar cane being crushed between rollers.

The juices of the sugar cane are extracted by crushing the stalks between rollers (Fig. 170) and evaporating the liquid thus obtained in vacuum pans. In this way the solution boils at a low temperature (about 65° C.), and the *decomposition* of a part of the sugar is prevented. When the sirup cools the sugar crystallizes, and the crystals are separated from the liquid by centrifugal machines. This gives brown sugar, which is usually refined by being dissolved in water and passed in solution through boneblack. The purified sirup is again concentrated in vacuum pans (Fig. 171) and crystallized out. Sugar is extracted from the sugar beet in much the same way, and the product is identical with the cane sugar.

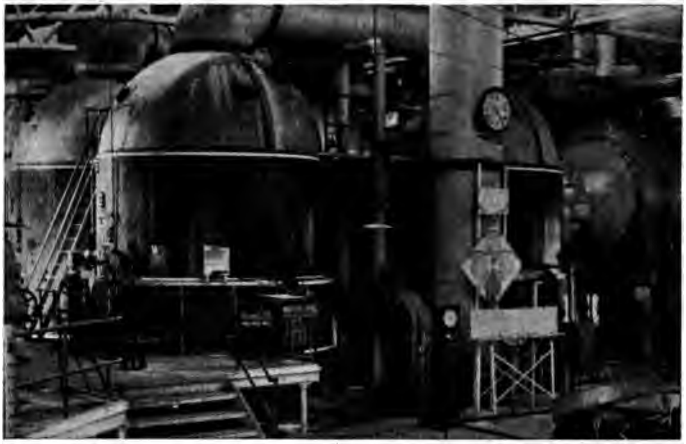

Fig. 171. Vacuum pans used to evaporate the sugar juice.

Since there are a great many different kinds of sugar we speak of ordinary sugar as **cane sugar**, or **sucrose**. When cane sugar is boiled with water and a little acid to act as a catalyst, it forms two simpler isomeric sugars, **glucose** and **fructose**; this case of hydrolysis is often called **inversion**:

$$\underset{\text{cane sugar}}{C_{12}H_{22}O_{11}} + H_2O \longrightarrow \underset{\text{glucose}}{C_6H_{12}O_6} + \underset{\text{fructose}}{C_6H_{12}O_6}$$

Both of these sugars have a sweet taste, but not so sweet as cane sugar, and they crystallize with difficulty. Thus a solution of cane sugar when boiled with the addition of a little acid or similar substance is converted into a sticky mass which will not crystallize, a fact which is taken advantage of in making different kinds of candy

281. Glucose, or grape sugar ($C_6H_{12}O_6$). This sugar occurs in many fruits and is often called grape sugar because of its presence in grape juice. It can be prepared from cane sugar or starch. The molecule of cane sugar is composed of a molecule of glucose and one of fructose joined together with the loss of water, in much the same way as an ester is formed from a molecule of alcohol and one of acid (§ 271). So too a molecule of starch is probably made up of a great many molecules of glucose and similar sugars linked together. When starch is boiled with very dilute acid it is broken down into glucose.

Let us boil a little starch with water into which have been put a few drops of hydrochloric acid to act as catalyst. Then we add enough sodium carbonate to neutralize the acid. The liquid is found to be sweet in taste because of glucose. We can test for glucose by adding Fehling's solution (§ 447), which gives a red precipitate of cuprous oxide (Cu_2O) on heating.

To understand the change of starch into glucose we must note that starch has such a large molecule that we do not even try to write an exact empirical formula for it. It is sometimes written as $(C_6H_{10}O_5)_x$ since we do not know its molecular weight. This merely shows the relative number of atoms in the molecule without giving their total number. In this reaction the water decomposes the large molecules and combines with the material:

$$\underset{\text{starch}}{(C_6H_{10}O_5)_x} + x\,H_2O \longrightarrow x\,\underset{\text{glucose}}{C_6H_{12}O_6}$$

We have here an example of hydrolysis.

This method is used commercially on a large scale for preparing glucose. The material is usually sold as a thick sirup under the name of **glucose**, or **corn sirup**, or as a mass of crystals. Glucose is used very extensively in the manufacture of jams, jellies, candies, and sirups. It is much cheaper than cane sugar and although not quite so sweet can be used in place of the crystalline sugar for most purposes.

282. Starch ($C_6H_{10}O_5$). Starch is the most abundant of the carbohydrates. It is contained in large quantities in all grains and in potatoes. Starch is built up by plants from water and carbon dioxide under the influence of the energy from the sun. This is done in the plant through the agency of the green coloring material in the leaves, which is called **chlorophyll.** We do not know just how this remarkable synthesis takes place; it has been impossible to duplicate it in the laboratory. The sugars which occur in the sugar cane, the sugar maple, etc., are probably formed either by a similar synthesis, or else by the decomposition of some starch already formed by the plant.

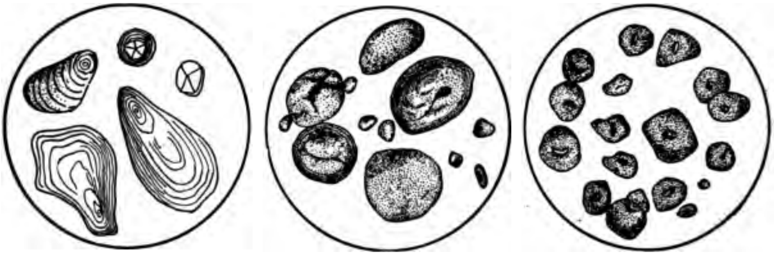
Potato *Wheat* *Corn*

Fig. 172. Starch grains, greatly magnified.

Starch is usually obtained for commercial purposes from the potato or from corn. It is present in vegetable material as small granules, which are often incased in fibrous material. The cellular structure of the vegetable is broken up by grinding; the particles of starch are then washed away by a stream of water and collected. Starch is insoluble in cold water but goes into solution in hot water, forming a colloidal solution. These colloidal solutions are used in the laundry for stiffening purposes.

The minute **granules of starch** differ somewhat in appearance (Fig. 172) according to the source of the starch. It is possible with a microscope to determine from what plant any particular sample of starch was obtained. Since it is the main constituent of potatoes and all the grains, it enters very largely into the food of man. These starchy foods are made more digestible by cooking because in that process the starch granules burst. But before starch can be assimilated in the human body it must be converted into the simpler sugars by the action of the digestive juices.

The **alcoholic fermentation of grain**, of which we spoke in the last chapter, starts with starch. The starch is changed into sugar by the action of water in the presence of a catalyst which occurs in sprouting barley. Catalysts found in living material are called **enzymes**. It is usual to bring the grain or other source of starch into contact with some sprouted barley. By the action of the enzyme the starch is thus converted into a sugar. Yeast is then added, and the alcoholic fermentation of the sugar takes place.

283. Cellulose ($(C_6H_{10}O_5)_n$). Cellulose is the principal material in the woody fiber of plants. Linen, cotton, hemp, and flax are chiefly cellulose. Absorbent cotton and the ordinary filter paper used in the laboratory are almost pure cellulose. This substance is another carbohydrate and has the same chemical composition as starch. We know nothing about the size of its molecules, but it is evidently more complicated than starch; so we write it as $(C_6H_{10}O_5)_n$. It is insoluble in water and most other solvents. When boiled with acids it is hydrolyzed into simple sugars like glucose.

284. Fabrics and paper. Vegetable fabrics like **cotton, linen**, and **jute** are composed of cellulose. The particular form in which this cellulose has been produced by the plant determines the nature of the thread and fabric. Paper is largely made from the cellulose obtained from wood, although the finer grades are manufactured out of linen and cotton rags.

Wood is composed of a rather impure form of cellulose, but in the manufacture of paper some of these impurities, which are colored resinous materials, are removed after the wood has been reduced to a pulp. When this wood pulp is rolled out into thin sheets and dried

(Fig. 173), we have a porous paper, such as filter paper, which is fairly pure cellulose. In order to make a paper that is suitable for writing and printing, the pulp is mixed with a number of inorganic solids such as clay and chalk; these substances are called fillers and lend rigidity and body to the paper. Most papers are given a smooth coating by treating them with some substance like casein (from milk), which can be ironed into the hard surface necessary for writing and printing.

Cheap paper is made from so-called "mechanical pulp." This is wood which has merely been ground to a pulp by a sort of grindstone. Such paper contains most of the original impurities of the wood and soon turns yellow and becomes brittle. Better grades of paper are made from pulp which has been purified by treatment with sodium hydroxide, bleaching powder, or sodium sulfite. These chemicals remove the impurities from the cellulose.

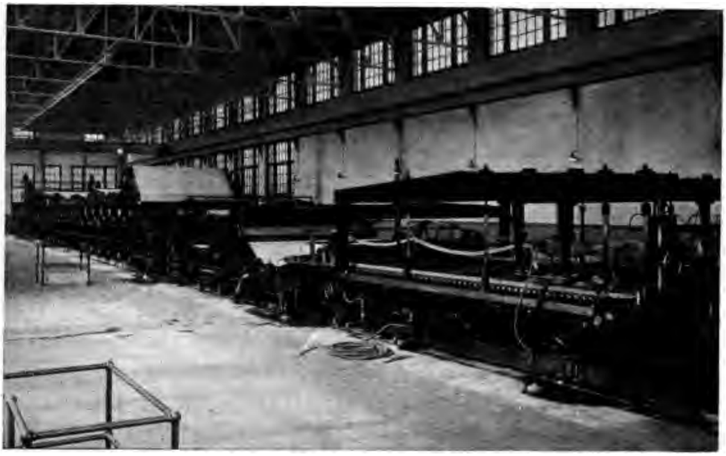

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Fig. 173. Paper-making machine.

Paper made from mechanical pulp gives a yellow color when treated with a water solution of aniline (a benzene derivative, $C_6H_5NH_2$). Newspapers and wrapping papers will give this test; writing paper *usually will not.*

The animal fabrics, **silk** and **wool**, are not carbohydrates. They are complex nitrogen compounds. The essential difference between the appearance of silk and cotton is, however, due to the mechanical structure of the fiber and not to its chemical constitution. Figure 174 shows the difference between these fiber structures. A thread of silk is one continuous, long tube, which causes the well-known appearance of silk material. Cellulose can be converted into a long fiber which somewhat resembles that of silk. This is done by dissolving it in certain solvents and then squirting the solution through a very fine hole into a second solution which immediately causes the cellulose to be reprecipitated in the form of a fine, long, continuous thread. When these threads are woven into a fabric, the product closely resembles pure silk and is called artificial silk. The material is, however, still cellulose.

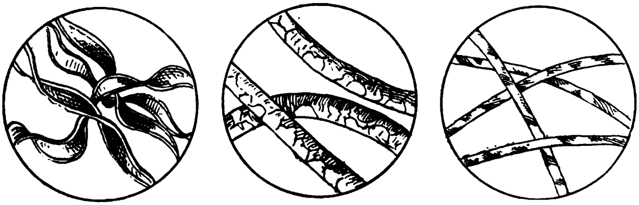
Cotton *Wool* *Silk*

Fig. 174. Three textile fibers, greatly magnified.

Mercerized cotton is made by treating cotton cloth under tension with sodium hydroxide. After washing and drying, the cloth has a somewhat silky appearance and is stronger than ordinary cotton cloth.

285. Nitrocellulose. When cellulose is treated with a mixture of sulfuric and nitric acids, it forms an ester of cellulose and nitric acid. This action probably takes place because of a certain number of hydroxyl groups which are present in the cellulose molecule. According to the concentration of the acid and the way in which the reaction is carried out, a varying amount of nitric acid can be made to react with the cellulose. The products are called **nitrocellulose**.

Nitrocellulose which contains relatively little nitrogen (called the **lower nitrates**) is used in the preparation of smokeless powder (§ 241). **Collodion** is a solution of the lower nitrates in a mixture of alcohol and ether. When these solvents evaporate, they leave a thin film of material, which is used for coating photographic plates and for similar purposes. Collodion is often sold under the trade name of "**new-skin**" or "**liquid court-plaster.**" **Celluloid** is made by heating a mixture of camphor and nitrocellulose. It is consequently very inflammable and ignites with almost explosive violence. The **higher nitrates** are called **guncotton** and are used as the explosive in torpedoes.

FATS AND OILS

286. Fats and oils are esters. Both plants and animals form a number of substances which are classed as **fats** and **oils.** The plant products are usually liquids and are called oils; for example, olive oil and cottonseed oil. Similar substances which are made in the animal body from the vegetable oils which it consumes are semi-solids and are called fats, such as butter and lard. *These substances are all esters of organic acids and glycerin.* For example, stearin is the principal fat in tallow; it has the formula $C_3H_5(C_{18}H_{35}O_2)_3$. It is derived from glycerin ($C_3H_5(OH)_3$) and stearic acid ($C_{17}H_{35}COOH$).

287. Drying oils. One common use of the vegetable oils appears in the manufacture of paints and varnishes. Most important for this purpose is **linseed oil**, which is obtained by squeezing the oil from certain seeds. The acids of which linseed oil is the ester contain less hydrogen than the corresponding fatty acids. If we should write out their formula we should find that, like ethylene, they contain carbon atoms linked together by double bonds. Compounds of this sort which are deficient in hydrogen are called **unsaturated compounds.** In linseed oil these unsaturated esters have the *property of combining* with the oxygen of the air. This process of oxidation results in the formation of a very tough, impervious, but transparent substance. It takes place when we spread a thin coat of linseed oil on a piece of wood and leave it for a few days. We speak of it as **drying**, but the process is really *not drying* in the usual sense of the word but *oxidation*. Paints are suspensions of colored materials in linseed oil; when this mixture is exposed to the air, the oil is oxidized to a thin, hard coating which is colored by the suspended materials called **pigments**. Certain oxides, like red lead (Pb_3O_4), facilitate the oxidation of the oil and are often mixed with the paint in order to cause it to *oxidize more quickly*. Such substances are spoken of as **dryers**.

288. Edible oils. Fats and oils are used extensively as foods. For a great many culinary purposes it is necessary to have a solid fat; hence the animal fats are used in cooking to the almost complete exclusion of the vegetable oils. The only difference between these compounds is a few hydrogen atoms more or less. Recently a process has been devised by which these hydrogen atoms can be added artificially. The vegetable oil is heated and mixed with a certain catalyst, usually finely divided nickel. Hydrogen gas is then blown through the mixture and under the influence of the catalyst is absorbed by the unsaturated oil, thus producing the ester of a fatty acid with a much higher melting point. The nickel is filtered off while the mixture is still hot. On cooling, the mass sets to a solid which in every way resembles an animal fat. This process is called the **hydrogenation of oils.**

Olive oil consists mainly of olein ($C_3H_5(C_{18}H_{33}O_2)_3$) and palmatin ($C_3H_5(C_{16}H_{31}O_2)_3$); **lard** is prepared from the fat of the hog and contains stearin in addition to palmatin and olein. **Beef tallow** is a solid fat which is mainly stearin. These materials have become so expensive that various mixtures of beef fat and cottonseed oil are now used in cooking under such names as Cottolene. It is further possible by hydrogenation to convert cottonseed oil into a hard solid, which is sold as Crisco and other lard substitutes. Fish oils can be converted into oils suitable for making soaps.

Foods

289. Uses of different kinds of foods. The food we eat serves *three distinct purposes:*

(1) To build up new parts and replace worn-out ones;
(2) To keep the body at the required temperature;
(3) To supply the energy which enables us to work.

It is convenient to divide our foods into four classes according to their composition and the purposes they serve. The **carbohydrates**, such as starch and sugar, furnish both heat and body energy and also assist in building fats in the body. The **fats** — for example, butter, meat fat, and olive oil — produce both heat and energy. To some extent they form layers of protective tissue which may serve as a reserve food supply. The **proteins**, which are chemically very complex substances, are *foods rich in nitrogen;* for instance, lean meat and the white of eggs. These replace the worn-out muscle tissue. The proteins have recently been carefully studied by the German chemist, Fischer (Fig. 175). Finally, various **mineral compounds** are needed in the body to serve a great variety of uses. The quantities of iron, chlorine, sulfur, phosphorus, calcium, magnesium, sodium, and potassium which are required are extremely small. These substances are *usually supplied in* common salt, meat, fruit, and vegetables.

FIG. 175. EMIL FISCHER (1852–1919). Brilliant organic chemist, who added much to our knowledge of the carbohydrates and proteins.

290. Value of food. Many articles of food contain compounds which represent all four classes of food substances, but the proportion of carbohydrates, fats, and proteins in them varies greatly (Fig. 176). Milk probably contains all of these food substances in about the proportion in which they are needed in the body. The composition of cow's milk averages approximately as follows:

Water	87.2%
Casein (nitrogenous matter)	3.6%
Butter fat	3.6%
Lactose (milk sugar)	4.9%
Mineral matter	0.7%

It is the casein which is used in the manufacture of *cheese.* When milk sours the lactose changes by fermentation to *lactic acid.* This change is brought about by certain bacteria.

Since foods act partly as fuels to supply the necessary heat and energy, we may determine their heat value very much as we determine the heat value of coal. The following table taken from Sherman's "Chemistry of Food and Nutrition" shows the percentage composition and fuel value in Calories[*] per pound of the edible portion of a few common foods.

	WATER	CARBOHYDRATE	FAT	PROTEIN	ASH	FUEL VALUE
Apples	84.6	14.2	0.5	0.4	0.3	285
Bacon	20.2		64.8	9.9	5.1	2840
Bananas	75.3	22.0	0.6	1.3	0.8	447
Beans, dried	12.6	59.6	2.9	22.5	3.5	1565
Beef, round steak	73.8		7.9	22.1	1.2	694
Bread, white	35.3	53.1	1.3	9.2	1.1	1199
Butter	11.		85.0	1.0	3.0	3491
Corn, green	75.4	19.7	1.1	3.1	0.7	455
Eggs	73.7		10.5	14.8	1.0	672
Oatmeal	7.3	67.5	7.2	16.1	1.9	1811
Potatoes	78.3	18.4	0.1	2.2	1.0	374
Tomatoes	94.3	3.9	0.4	0.9	0.5	104

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[*] The Calorie used here is the large Calorie, which is the amount of heat required to raise the temperature of 1 *kilogram* of water 1° C.

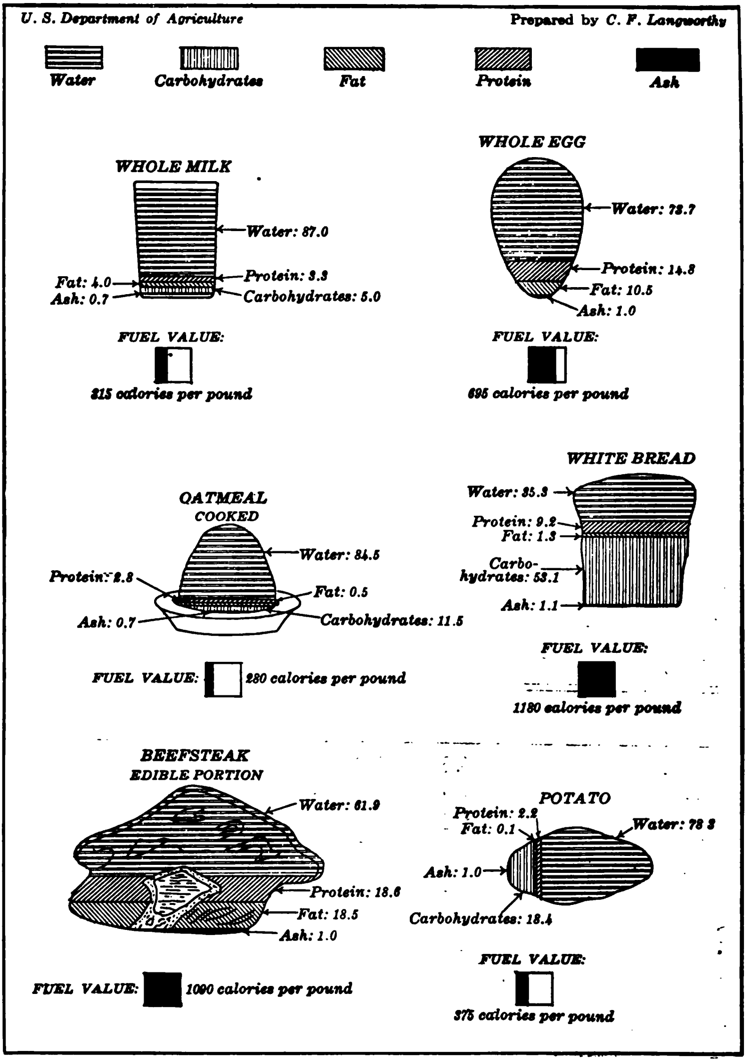


Fig. 176. **Diagram to show the proportion of carbohydrates, fats, proteins, and water in some common articles of food.**

291. How much food do we need? In recent years an immense amount of experimental study has been devoted to this subject, and the authorities do not altogether agree in their results. In general, however, it is considered that the total energy value of an adult diet should be not less than 3000 Calories a day. It is evident, of course, that this value will depend somewhat on the nature of the work which one is doing. Then, too, there are many other factors which affect the process of digestion but which are difficult to measure, such as the appetizing character of the food and the nervous condition of the person.

The amount of protein required for building up and replacing the worn-out parts of the body is probably a great deal less than that consumed in our usual diet; the balance of the protein food which we eat is merely consumed as fuel. It must not be thought that the proteins alone supply the material for replacement and growth. Both fats and carbohydrates are also concerned in this process although their chief use is to supply energy. It would seem as if 75 grams (about 3 ounces) of protein per day were sufficient for the average adult; this is much less than most of us eat.

292. Accessory factors. In addition to the foods that we have considered, the animal system must also have an adequate supply of water and inorganic salts, which are obtained without difficulty in the food. Recently a great deal of interesting evidence has been accumulated showing that very minute amounts of certain compounds seem also to be essential to the growth and healthy condition of animals. These substances have been called **accessory factors in the diet**; they have not yet been definitely identified or isolated, although in certain cases they are nitrogen compounds which have been called "vitamines." They appear to be substances analogous to catalysts. Certain diseases, such as *beri-beri* and *scurvy,* have been shown to be due to their absence in the diet. In general, it can be said that a widely distributed diet will insure a sufficient supply of these accessory factors.

Because of the extreme complexity of the reactions which go on in the body, the whole problem of nutrition is a very difficult one. The heat values of foods, such as those shown in the table, are of some help in determining the proper diet; but one must obviously be very careful in drawing any conclusions from such inadequate data. These energy values do not take into account the protein requirement, the digestibility of the food stuff, or the need and importance of accessory factors.

SUMMARY OF CHAPTER XXIV

NO ESSENTIAL DIFFERENCE exists between organic and inorganic compounds. Many organic compounds may be prepared in the laboratory from inorganic material.

CARBOHYDRATES are compounds which contain carbon combined with hydrogen and oxygen in the proportion in which they occur in water. Sugar, starch, and cellulose are important carbohydrates.

ORDINARY SUGAR is made from sugar cane or sugar beet. On being boiled with water in the presence of an acid it is hydrolyzed into *glucose* and *fructose*.

STARCH is obtained commercially from corn or potatoes. Starch may be broken down into glucose by dilute acids, or by an enzyme in sprouting barley. This change is brought about before the alcoholic fermentation of grains and starch.

CELLULOSE is a carbohydrate which constitutes the fibrous material of plants. Cotton, linen, and paper are mainly cellulose, but wool and silk are not.

NITROCELLULOSE is made by the action of nitric acid on cellulose. It is the basis for smokeless powder, collodion, and celluloid.

FATS AND OILS are the glycerin esters of organic acids. Drying oils are oxidized in drying. Vegetable oils differ from animal fats by only a few hydrogen atoms, which can be added artificially by means of a catalyst.

FOODS serve (1) as fuel to supply energy for doing work, (2) as fuel to keep the body warm, and (3) to furnish material to repair worn-out and growing parts.

FOUR CLASSES OF FOODS are *fats*, *carbohydrates*, *proteins*, and *mineral compounds*. Fats and carbohydrates furnish primarily the necessary energy. Proteins (nitrogen compounds) are essential to growing organisms and are necessary for replacing wear and tear.

THE AVERAGE ADULT needs food which will furnish about 3000 Calories per day and which contains about 75 grams of protein, besides small but indispensable amounts of mineral compounds.

CERTAIN MINUTE AMOUNTS of substances have been found to be essential in the diet. These substances are called *accessory factors*.

QUESTIONS

1. How does a hydrocarbon differ in composition from a carbohydrate?

2. Why are vacuum pans used in concentrating sugar solutions?

3. How could you prove that a piece of filter paper contained carbon?

4. How would you test for the presence of grape sugar?

5. Describe the steps in the process of making alcohol from potatoes.

6. In preparing starch from corn, why is cold water used instead of hot?

7. What is the difference between sucrose and glucose? between collodion and celluloid?

8. What chemical process takes place when the paint dries on the side of a house?

9. What is the distinction between a fat and an oil?

10. What is the difference between oils made from petroleum and vegetable oils?

11. What is the danger in putting formalin into milk as a preservative?

12. Why should oatmeal be thoroughly cooked?

13. What difference should be made between summer and winter diets?

14. What difference should be made between the diet of a bank clerk and that of a blacksmith?

15. Name three articles of food which are rich in carbohydrates, in fats, in proteins.

16. Why is an abundant supply of pure water necessary for the digestion and assimilation of our food?

REVIEW QUESTIONS

1. Describe three allotropic forms of carbon. State how they are obtained. Give the uses to which they are put.

2. What is soap? How is it made? What is the difference between hard and soft soap?

3. How is ethyl alcohol prepared commercially? What agent effects the production of ethyl alcohol in this process?

4. How may nitric acid be made? Write the equation. State the properties of nitric acid.

5. (a) Outline one method of making concentrated sulfuric acid.
(b) Show how the properties of this product differ from those of dilute sulfuric acid.

6. Explain how the human body obtains energy from the sun.

TOPICS FOR FURTHER STUDY

Sugar. Has sugar always been an essential part of man's food? How is sugar obtained from the sugar cane and sugar beet? What is molasses? What familiar articles of food contain large amounts of glucose? How is it made, and is it a desirable food? Is saccharin a sugar? (*Slosson's* Creative Chemistry and *Martin's* Modern Wonders.)

Essential materials from wood and cotton. What is the chief constituent of wood fiber and cotton? What are some of the important things into which it can be converted? In what way has the printing press helped to deplete our forests? What is the chemical relationship of artificial silk, smokeless powder, "new skin," writing paper, and a photographic film? How is each made? (*Slosson's* Creative *Chemistry and Duncan's* Chemistry of Commerce.)

CHAPTER XXV

SODIUM AND POTASSIUM COMPOUNDS

Alkali metals — sodium chloride — hydroxide, preparation, properties, and uses — sodium carbonate, manufacture by Leblanc and Solvay processes — the two carbonates of soda, properties and uses — hydrolysis — other sodium compounds.

Potassium compounds — source and use as fertilizers — preparation of saltpeter — deliquescence. Metallic sodium and potassium — sodium peroxide — comparison with ammonium salts — flame tests — spectroscope.

293. General characteristics. The compounds of sodium and potassium are so much alike that they can conveniently be considered in the same chapter. The elements sodium and potassium are both metals with a valence of one, and form positive monovalent ions. They are not found in a free state in nature. All of their simpler compounds are soluble in water. Both metals form strong bases with water, and both form many useful compounds, which occur abundantly.

294. Sodium chloride, or common salt ($NaCl$). This substance occurs as large beds of rock salt, which are found mainly in the United States, Austria, and Germany. It also forms the major part of the dissolved material in sea water and in certain inland lakes, like Great Salt Lake and the Dead Sea. Salt for commercial purposes is obtained by mining rock salt and by the evaporation of sea water or the brine which is obtained from salt wells located near salt deposits. In certain places, such as on some of the shores of San Francisco Bay (Fig. 177), the sea water is run into shallow basins and is evaporated by the heat of the sun. In other places, as in Russia, the water is frozen out of the solution. But usually the solution is evaporated by heat under reduced pressure. The pure salt crystallizes out first and can, if necessary, be collected and recrystallized for further purification.

Sodium chloride is the source of all sodium compounds and is consequently of great importance to many industries (see Industrial Chart, page 205). A small quantity of salt is essential in the food of both man and beast; large amounts are used in preserving meat and fish and in making ice-cream. When it is to be used for industrial purposes, it is generally sold in the form of **rock salt**, which is made by crushing to a uniform size the lumps as mined. For cooking purposes and for the table it is sold as a fine crystalline powder. It is generally contaminated with a small quantity of calcium and magnesium chlorides, which readily absorb moisture from the air and cause the salt to stick together in lumps. Chemically pure salt, from which these impurities have been removed, does not absorb water from the air.

Fig. 177. Gathering salt from San Francisco Bay with the aid of a tractor.

295. Sodium hydroxide, or caustic soda (NaOH). We have already seen (§ 31) that when metallic sodium reacts with *water* hydrogen is evolved and a substance called sodium hydroxide is left in solution. Commercially it is prepared by one of two methods.

The **electrolytic method** consists in passing an electric current through a solution of sodium chloride. Sodium chloride in aqueous solution is ionized, as we know, into sodium (Na^+) and chlorine (Cl^-) ions. Therefore we find that the chlorine ions move toward the anode and are discharged with the liberation of free chlorine; and that the sodium ions move with the current toward the cathode and are there discharged, forming metallic sodium. But this in turn reacts with the water of the solution and forms sodium hydroxide with the liberation of free hydrogen. These reactions can be expressed as follows:

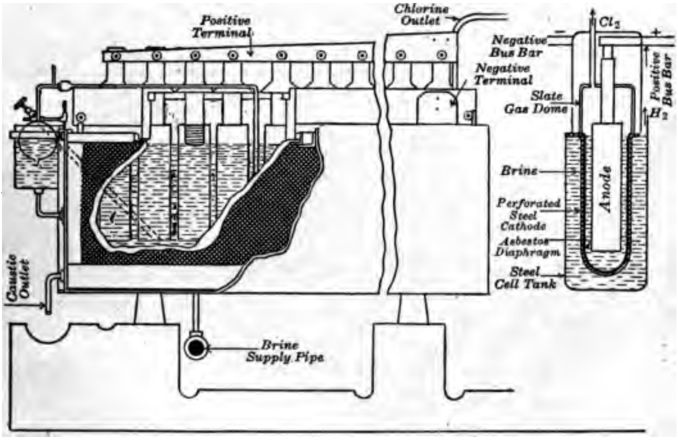


Fig. 178. Electrolytic cell for decomposing salt.

$$NaCl \longrightarrow Na^+ + Cl^- \text{ (in solution)}$$

At cathode $2\,Na^+ \longrightarrow 2\,Na$ At anode $2\,Cl^- \longrightarrow Cl_2$

$$2\,Na + 2\,H_2O \longrightarrow 2\,NaOH + H_2$$

If this process is carried out in one vessel the sodium hydroxide gradually diffuses back to the other electrode and reacts with the chlorine to form products which are not desired. Several different devices have been invented to obviate this difficulty. Perhaps the simplest of these involves the separation of the two electrodes by means of *porous asbestos*, as shown in figure 178. The carbon rods act as anodes and the perforated steel diaphragm as the cathode. A concentrated solution of salt is fed in near the positive electrode, and the sodium hydroxide solution, which is formed near the other electrode, is continually drawn off. The solution of sodium hydroxide is then evaporated at a high temperature and leaves sodium hydroxide in a molten condition. This can be cast into any desired shape.

In some factories (Fig. 179), such as paper mills, both bleaching powder and caustic soda are employed, and so immediate use can be made of all the products of this electrolysis of sodium chloride except the hydrogen. The chlorine produced at the anode is passed directly into calcium hydroxide to form " bleach."

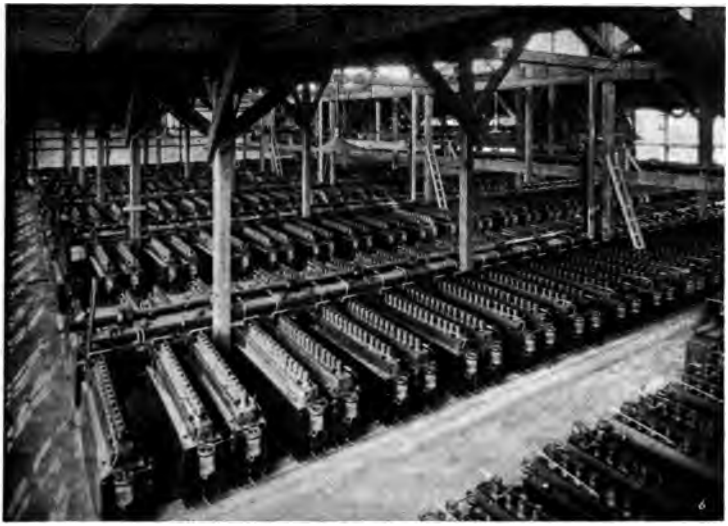


Fig. 179. Room containing several hundred cells, each of which is decomposing brine.

In the lime process sodium carbonate is treated with slaked lime; insoluble calcium carbonate and sodium hydroxide are formed:

$$Na_2CO_3 + Ca(OH)_2 \longrightarrow CaCO_3 \downarrow + 2\,NaOH$$

The calcium carbonate is filtered off and the solution evaporated as before.

296. Properties and uses of sodium hydroxide. This *substance is a white solid,* which for laboratory purposes is ordinarily sold in slender sticks, but for industrial uses as a solid mass in iron drums. It rapidly absorbs water and carbon dioxide from the air. When dissolved in water it is almost completely ionized and is therefore a *strong base.* Its solutions are used whenever hydroxyl ions are needed in the laboratory.

Concentrated solutions of sodium hydroxide and the moistened solid itself are very corrosive, hence the name **caustic soda.** It will quickly disintegrate most vegetable and animal material. In the household it is valuable for cleansing purposes because it reacts with and dissolves grease; it is sold in tin cans under the name **lye.** Sodium hydroxide is a very important substance in the industries; it is used in the manufacture of soap, in the refining of petroleum, and in the preparation of coal-tar products. (See Industrial Chart on page 205.)

297. The manufacture of sodium carbonate (Na_2CO_3). Formerly this substance was obtained from the ashes of sea plants and was called **soda ash.** In recent times the need for it has become so great that two methods have been devised for making it directly from salt.

The **Leblanc process** is the older and is still used in Europe. In this method sodium chloride and sulfuric acid react to produce hydrochloric acid and sodium sulfate (also called **Glauber's salt**):

$$2\,NaCl + H_2SO_4 \longrightarrow Na_2SO_4 + 2\,HCl\uparrow$$

The sodium sulfate is then reduced to the sulfide by heating with carbon:

$$Na_2SO_4 + 4\,C \longrightarrow Na_2S + 4\,CO\uparrow$$

The sodium sulfide is now treated in water solution with calcium carbonate, and the following reaction takes place:

$$Na_2S + CaCO_3 \longrightarrow CaS\downarrow + Na_2CO_3$$

The calcium sulfide (CaS) is relatively insoluble, and so the very soluble sodium carbonate can be dissolved away from it. In practice the process is shortened to two steps, the sodium sulfate being mixed with both coke and limestone. The last two reactions then go on together.

The principal by-product obtained is hydrochloric acid. If it were not for this valuable by-product, the Leblanc process could not hold its own in competition with the other important method of making soda.

In the United States the **Solvay process** is used almost altogether. At Syracuse, N. Y. (Fig. 180), the process is carried out on an enormous scale. The principle of the process can be explained in three steps:

[1] Ammonia and carbon dioxide are dissolved in water, forming ammonium bicarbonate (NH_4HCO_3).

[2] This in turn reacts with sodium chloride, giving sodium bicarbonate ($NaHCO_3$) and ammonium chloride. The sodium bicarbonate, being only sparingly soluble in this solution, is precipitated.

[3] Finally, the bicarbonate on heating forms the carbonate. The reactions are as follows:

$$NH_3 + CO_2 + H_2O \longrightarrow NH_4HCO_3 \qquad [1]$$

$$NH_4HCO_3 + NaCl \longrightarrow NaHCO_3\downarrow + NH_4Cl \qquad [2]$$

$$2\,NaHCO_3 \longrightarrow Na_2CO_3 + H_2O + CO_2 \qquad [3]$$

In the commercial process these reactions are carried out in the following manner: Brine from a salt well is saturated with ammonia gas and is then pumped into a carbonating tower. Carbon dioxide enters this tower at the bottom under pressure and is absorbed by the ammoniacal brine. The sodium bicarbonate comes down as a fine powder suspended in the liquid and is filtered off. The ammonium chloride is recovered from the solution by evaporation and is treated with lime in order to secure the ammonia for use again:

$$2\,NH_4Cl + Ca(OH)_2 \longrightarrow 2\,NH_3\uparrow + CaCl_2 + 2\,H_2O$$

In this way no ammonia is lost in the process. The carbon dioxide is obtained by heating limestone; the other product is calcium oxide, which gives with water calcium hydroxide:

$$CaCO_3 \longrightarrow CaO + CO_2\uparrow$$

$$CaO + H_2O \longrightarrow Ca(OH)_2$$

The calcium hydroxide is used for regenerating the ammonia as just

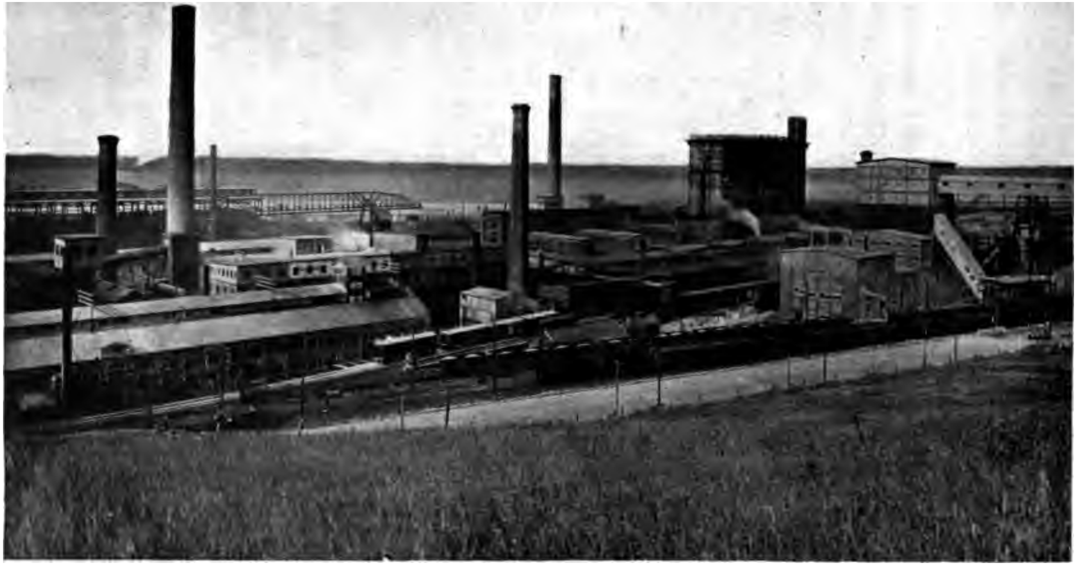


Fig. 180. General view of the Solvay works at Syracuse, N. Y.

described. Thus we see (Fig. 181) that in this process the raw materials are calcium carbonate (limestone) and sodium chloride, two substances which can be obtained very cheap and in large quantities. The two products are sodium carbonate and calcium chloride. The latter has very little value and is for the most part thrown away.

The Solvay process is much simpler and apparently more economical than the Leblanc process, which, as we have said, is still used because of the value of the hydrochloric acid produced in the first step. *Such a product which is not the main object for which the process is carried out is called a* ***by-product.*** Many manufacturing operations are made financially possible by the production of one or more valuable by-products.

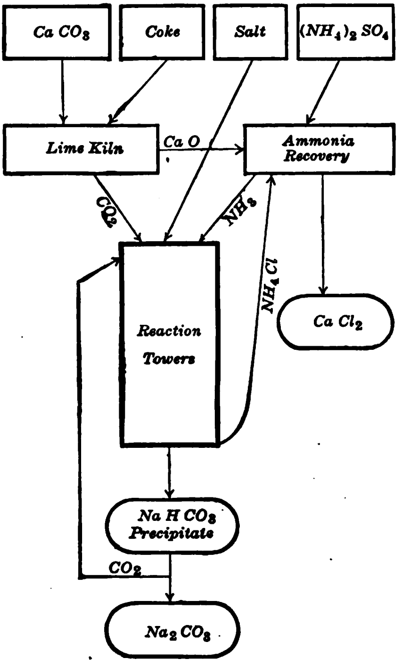


Fig. 181. Diagram of the Solvay process.

298. The two carbonates of soda. Sodium carbonate forms large crystals containing ten molecules of water ($Na_2CO_3 \cdot 10\ H_2O$). It is very soluble in cold water. Sodium bicarbonate ($NaHCO_3$) (sometimes called sodium hydrogen carbonate) is a fine, white, crystalline powder which is only sparingly soluble in water. When a solution of sodium carbonate in water is saturated with carbon dioxide, sodium bicarbonate is precipitated:

$$Na_2CO_3 + H_2O + CO_2 \longrightarrow 2\ NaHCO_3$$

The reverse of this reaction takes place when sodium bicarbonate is heated, as in the last step of the Solvay process. Both substances react readily with acids, forming a salt and carbonic acid. Since carbon dioxide is but slightly soluble in water the carbonic acid decomposes and the gas escapes; for these reasons the reaction runs practically to an end:

$$NaHCO_3 + HCl \longrightarrow NaCl + H_2O + CO_2$$

$$Na_2CO_3 + 2\ HCl \longrightarrow 2\ NaCl + H_2O + CO_2$$

Because the carbonates will react with acids, producing salts, they can be used instead of a hydroxide for neutralizing an acid. They are also used as a source of carbon dioxide. The fire extinguisher described in section 67 contained a solution of sodium bicarbonate.

299. Baking powders. Sodium bicarbonate is also an essential component of baking powders; hence it is often called baking soda, or sal soda. The other necessary ingredient of baking powders is some solid substance which is weakly acidic, such as cream of tartar, calcium acid phosphate, or alum. When the carbonate and the acid become wet, there is a reaction which results in a large volume of carbon dioxide gas, which leavens the dough. In some cases sour milk is used instead of the solid acid. Here the lactic acid reacts with the carbonate. Baking powders usually contain a small amount of starch or flour to keep them from deteriorating. In making so-called raised bread, yeast is used, which reacts with the sugar in the dough and by alcoholic fermentation produces carbon dioxide gas.

300. Sodium carbonate, or washing soda (Na_2CO_3). Sodium carbonate is often called washing soda because it acts as a mild alkali and yet is not so alkaline as to injure seriously the flesh or fabrics. Sodium carbonate is used in enormous quantities in the manufacture of caustic soda, soap, and glass. (See Industrial Chart on page 205.)

Some of the sodium carbonate is put on the market as a dry powder, but another large part is sold as the so-called **soda crystals** ($Na_2CO_3 \cdot 10\,H_2O$). These crystals are transparent and contain ten molecules of water. They slowly crumble to a white powder consisting of the more or less dehydrated substance. This is an example of the process of **efflorescence.**

301. Hydrolysis. The reason why water solutions of sodium carbonate show an alkaline reaction when tested with litmus is easily seen if we consider the ionic reactions involved. Water is very slightly dissociated into H^+ and OH^- and, although we have hitherto disregarded this dissociation, we now find it to be of importance. The carbonate ion (CO_3^{--}) combines with a certain number of hydrogen ions (H^+) from the water and thus produces carbonic acid (H_2CO_3). This is a very weak acid and is only very slightly dissociated; hence a number of undissociated carbonic acid molecules are formed in the solution, as shown in the following equations:

$$H_2O \rightleftharpoons H^+ + OH^-$$

$$Na_2CO_3 \rightleftharpoons 2\,Na^+ + CO_3^{--}$$

$$2\,H^+ + CO_3^{--} \rightleftharpoons H_2CO_3$$

For every ion of hydrogen which is thus removed by the formation of the undissociated molecules, there is left a hydroxyl ion in the solution. The result is that a solution of sodium carbonate contains a greater number of hydroxyl ions than hydrogen ions. Therefore it reacts alkaline, but only feebly so, for the concentration of the hydroxyl ions is necessarily small since they can be formed only to the extent that undissociated carbonic acid is produced. *The action of the ions of water on a dissolved salt is called* ***hydrolysis***. It takes place whenever we are dealing with *the salt of a weak acid and a strong base, and results in an* ***alkaline*** *solution.* The weaker the acid, the more alkaline will the solution be.

It is interesting to note in this connection that the solution of sodium bicarbonate, often called acid sodium carbonate, reacts neutral with litmus.

We also have hydrolysis in the case of salts which are formed from a *strong acid and a weak base.* Here a certain concentration of undissociated base is produced, and an equivalent amount of hydrogen ions are set free, giving an **acid** reaction to the solution; thus, ammonium nitrate, copper sulfate, and zinc chloride solutions all react acid with litmus.

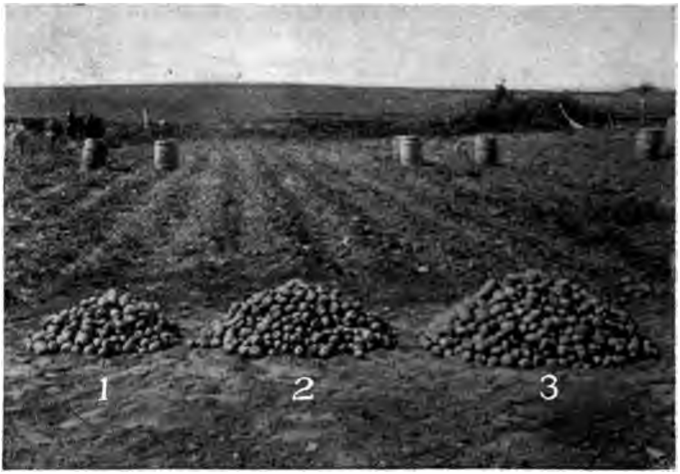
Salts of strong acids and strong bases are not hydrolyzed, and the solutions give a ***neutral*** *reaction.* Such salts are sodium chloride, potassium nitrate, sodium sulfate.

302. Other important compounds of sodium. We have already described (§ 218) **sodium nitrate** as that valuable natural nitrate which is used as a source of nitric acid and as a fertilizer. A second important compound, called sodium thiosulfate ($Na_2S_2O_3$), is made by boiling a solution of sodium sulfite with sulfur. The hydrate is known as "**hypo**" ($Na_2S_2O_3 \cdot 5\,H_2O$) and enters extensively into the fixing process of photography and into the bleaching industry. Another salt is **sodium cyanide** (NaCN), a white solid with a strongly alkaline water solution. It is extensively used in extracting gold because it dissolves that metal in the presence of air. The compound itself is extremely poisonous, and in contact with acids evolves *the very poisonous hydrocyanic, or prussic, acid* (HCN), which is sometimes used to exterminate vermin.

303. Potassium compounds. Potassium compounds are very similar to sodium compounds; we need consider them only very briefly. In general they are somewhat more soluble than sodium compounds and are therefore often preferred in the laboratory. Since they are more expensive, however, they are not used in the industries when the corresponding sodium salt will serve as well.

Potassium compounds are very widely distributed. They occur as the constituents of many igneous rocks, but these rocks are not suitable sources for obtaining the compounds commercially.

304. Potassium salts as fertilizers. In Chapter XXI we saw that nitrogen compounds were essential to the growth of plants. Potassium compounds are no less important in this regard. Most artificial fertilizers contain potassium salts, and the results of experiments like those shown in figure 182 prove that they are a valuable plant food. When plants are burned the potassium compounds are converted into potassium carbonate, which is found in the ashes. Thus wood ashes return needed potassium salts to the soil. By extracting wood ashes with water, potassium carbonate is produced. This was the old way of preparing potassium carbonate, which was called **potash.**



Courtesy of *Soil Fertility Lab., U. S. Dept. of Agr.*

Fig. 182. A U. S. government experiment showing the effect of fertilizers on potatoes: 1, fertilizer lacking potassium salts; 2, no fertilizer; 3, fertilizer containing potassium salts.

Since potassium compounds must be applied to the soil in order to produce the best crops, the question of the manner of obtaining them is vital. Potassium chloride is found in large deposits of mixed salts at Stassfurt, Germany, and this has hitherto been the principal source of supply, although other natural deposits have been found in certain places (*e.g.* in Utah) and have been used to a small extent. When the recent war cut off the Stassfurt supply, considerable quantities of potassium compounds were produced in this country from our own mineral deposits, from the cement industry, in which they are a valuable by-product, and from the ash of one or two giant algæ of the California coast. Strangely enough, although most sea plants contain sodium compounds rather than potassium compounds, these algæ are an important exception.

305. Important potassium compounds. Potassium hydroxide, or caustic potash (KOH), is prepared exactly as sodium hydroxide and resembles this substance in its physical and chemical properties. In the laboratory it is used instead of sodium hydroxide for a few special purposes, but in general the reactions of the two are identical. Potassium carbonate and bicarbonate are very much like the corresponding sodium compounds, except that the bicarbonate is very soluble in water. For this reason potassium carbonate cannot be prepared by the Solvay process but must be manufactured by the Leblanc process. Since the compounds of potassium are more expensive than those of sodium they find only limited uses aside from that as fertilizers.

Potassium nitrate (KNO_3) is commonly called **saltpeter.** It is usually prepared from sodium nitrate by the following reaction:

$$NaNO_3 + KCl \longrightarrow NaCl + KNO_3$$

When hot saturated solutions of sodium nitrate and potassium chloride are brought together, the sodium chloride is precipitated and can be filtered off, leaving potassium nitrate in solution with only a little sodium chloride. The solution can then be cooled and the potassium nitrate crystallized out. This reaction depends upon the solubilities of the substances involved at various temperatures; the relationship is best shown by the curves given on page 152.

306. Deliquescence. The chief use of potassium nitrate appears in the manufacture of gunpowder. For this purpose it is better than sodium nitrate because the latter tends to absorb moisture from the air and so makes it difficult to keep the gunpowder dry. There are a large number of salts which resemble sodium nitrate in their tendency to take up water from the air. This property of certain substances is called **deliquescence.**

307. Metallic sodium and potassium. Metallic sodium is prepared by the electrolysis of fused sodium hydroxides. This operation was first carried out by Sir Humphry Davy (Fig. 183).

FIG. 183. SIR HUMPHRY DAVY (1778–1829).

Brilliant English investigator who discovered sodium and potassium and invented the safety lamp used by miners.

In the iron apparatus shown in figure 184 the molten sodium hydroxide conducts the current just as a solution of the substance does; oxygen is liberated at one electrode and the metallic sodium and hydrogen at the other. In the fused hydroxide, however, the metallic sodium finds no water with which to react and can be obtained in the free state. It is lighter than the fused hydroxide, floats to the top in a molten condition, and is ladled off from time to time. Metallic potassium is made in exactly the same way.

Both metallic potassium and metallic sodium are very active substances and can be kept only if out of contact with the air. They are usually preserved under some such liquid as kerosene. When freshly cut both metals are silver white and very soft. They combine with most of the nonmetallic elements, such as oxygen and chlorine, with great energy. The *reaction with water* has already been discussed (§ 31). In the case of potassium the reaction is so violent that a piece of the metal takes fire when it is dropped on water.

308. Sodium peroxide. When metallic sodium is heated in air, it produces an oxide known as sodium peroxide (Na_2O_2). This oxide contains one atom more of oxygen than the normal oxide of sodium, and is a vigorous oxidizing agent; for that reason it finds many uses. Sodium peroxide reacts with water to form oxygen and thus furnishes a very convenient method of generating oxygen in the laboratory. Metallic sodium is prepared on an industrial scale for the preparation of this substance.

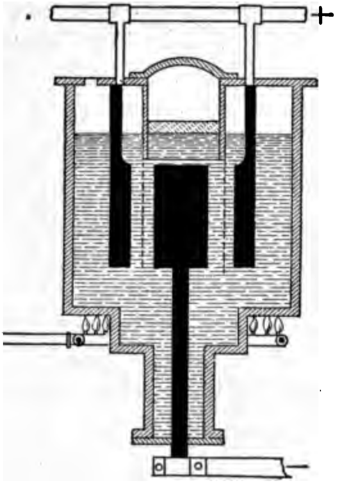


Fig. 184. Electrolytic cell for making metallic sodium.

309. Comparison with ammonium compounds. In Chapter XIX we studied the common compounds of ammonium (NH_4), such as the hydroxide, chloride, sulfate, and nitrate. These compounds are very similar to the corresponding compounds of sodium and potassium, in that the salts are white solids and are soluble in water, and in that the ammonium radical forms a monovalent positive ion.

310. Flame tests for sodium and potassium. Since all sodium and potassium compounds are soluble in water, we cannot test for them by any precipitation reaction. There is, however, one test for these elements which is extremely sensitive and which distinguishes them absolutely from every other substance. This is the color of the light which all sodium and potassium compounds, as well as the elements themselves, give out when they are heated to a high temperature.

We may hold a piece of clean platinum wire in the blue flame of a burner until all color disappears from the flame (Fig. 185). It may be necessary to use a new burner to avoid impurities. We touch the wire to a sodium salt and bring it again to the edge of the flame. Then we repeat the experiment using a pure salt of potassium.

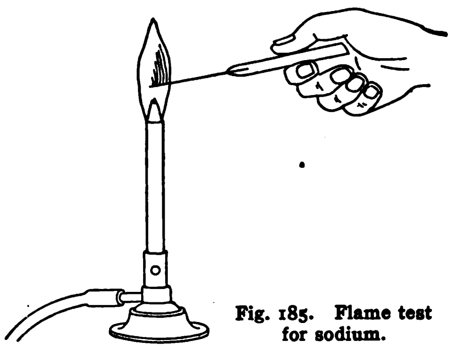


Fig. 185. Flame test for sodium.

The yellow color is a test for sodium. This is so delicate a test that all the flames in a laboratory where sodium salts are being used show traces of yellow color.

Potassium compounds color a similar flame ***purple.*** This color is a **test** for potassium and its compounds but is easily obscured by the yellow color due to a trace of sodium. To obviate this difficulty the flame may be observed through a blue glass, which cuts out the yellow light and enables us to see the potassium flame if it is present.

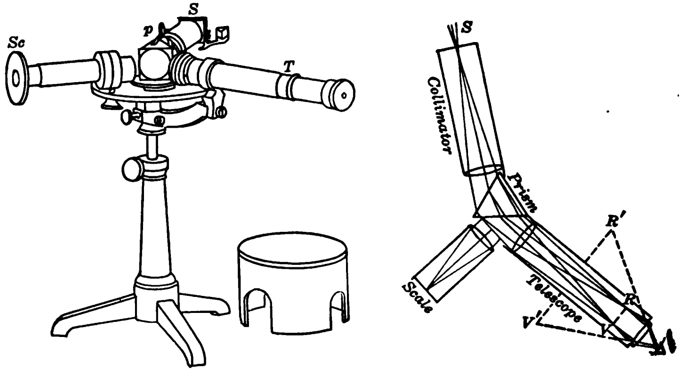
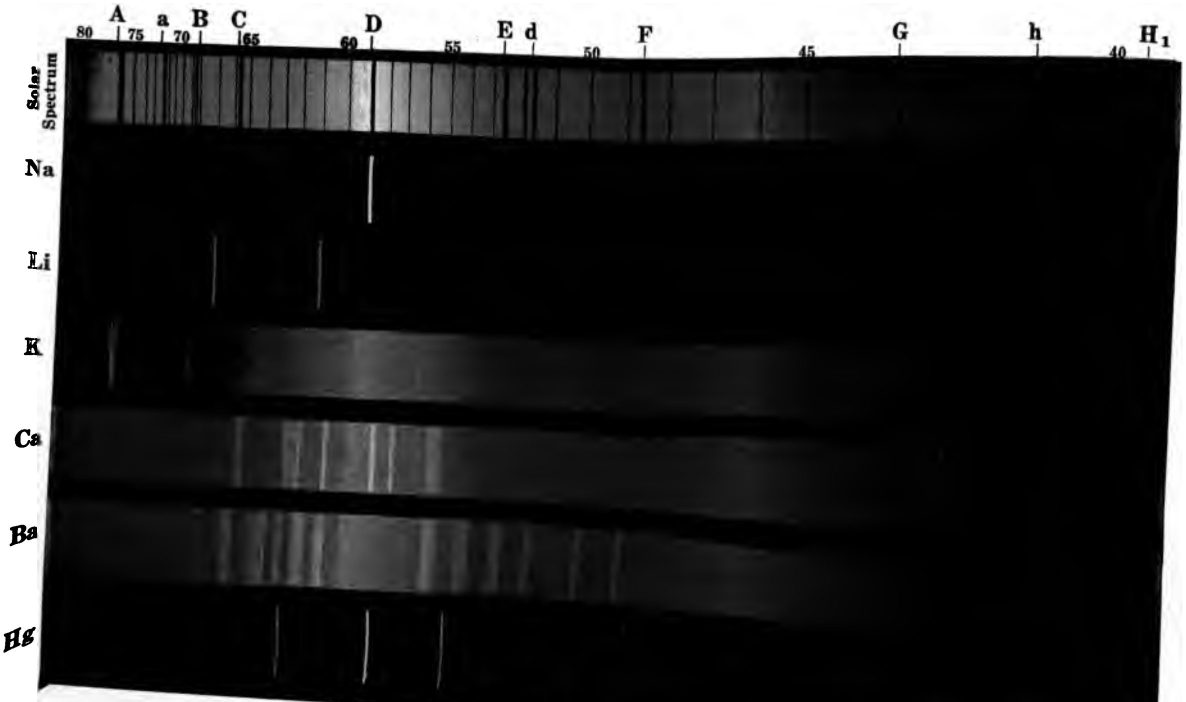


Fig. 186. Bunsen spectroscope.



SPECTRUM CHART.

We may hold a piece of clean platinum wire in the blue flame of a burner until all color disappears from the flame (Fig. 185). It may be necessary to use a new burner to avoid impurities. We touch the wire to a sodium salt and bring it again to the edge of the flame. Then we repeat the experiment using a pure salt of potassium.

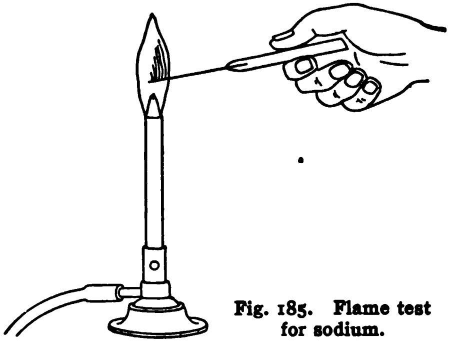


Fig. 185. Flame test for sodium.

The yellow color is a test for sodium. This is so delicate a test that all the flames in a laboratory where sodium salts are being used show traces of yellow color.

Potassium compounds color a similar flame purple. This color is a **test** for potassium and its compounds but is easily obscured by the yellow color due to a trace of sodium. To obviate this difficulty the flame may be observed through a blue glass, which cuts out the yellow light and enables us to see the potassium flame if it is present.

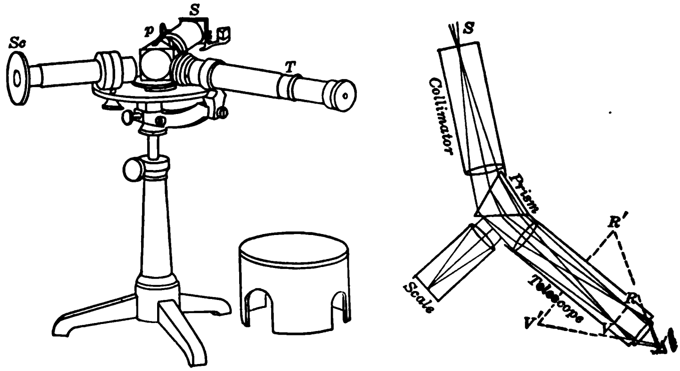


Fig. 186. Bunsen spectroscope.

311. Use of the spectroscope. A more exact method of testing for sodium and potassium is furnished by the spectroscope (Fig. 186). This instrument analyzes the light from the flame by means of a glass prism and shows a sharp, bright yellow line when sodium is present, even though the flame may be at the same time colored by more than this one substance. Other substances show characteristic lines when examined in this way (see Spectrum Chart). Some of them have a great many lines of varied colors; but none of the lines from different elements coincide exactly, and thus the presence of several elements in the same substance can be detected. This method of analysis was used by Bunsen (Fig. 187) and Kirchhoff in discovering two new elements which resembled sodium and potassium, namely, cesium and rubidium.

Fig. 187. Robert Wilhelm Bunsen (1811-1899).

Famous German chemist who invented the spectroscope and the burner used in the laboratory.

When the solar spectrum is studied carefully, we find that it is crossed by many vertical dark lines (see Spectrum Chart). These lines are called Fraunhofer lines and are caused by the presence in the outer layer of the sun's atmosphere of many gaseous elements which absorb certain characteristic portions of the light. The same effect may be observed in the laboratory if a beam of white light is passed through a sodium flame and then into a spectroscope; a dark line will be seen which is in the same place in the spectrum as the [illegible] line of the sodium spectrum.

311. Use of the spectroscope. A more exact method of testing for sodium and potassium is furnished by the spectroscope (Fig. 186). This instrument analyzes the light from the flame by means of a glass prism and shows a sharp, bright yellow line when sodium is present, even though the flame may be at the same time colored by more than this one substance. Other substances show characteristic lines when examined in this way (see Spectrum Chart). Some of them have a great many lines of varied colors; but none of the lines from different elements coincide exactly, and thus the presence of several elements in the same substance can be detected. This method of analysis was used by Bunsen (Fig. 187) and Kirchhoff in discovering two new elements which resembled sodium and potassium, namely, cæsium and rubidium.

FIG. 187. ROBERT WILHELM BUNSEN (1811–1899).

Famous German chemist who invented the spectroscope and the burner used in the laboratory.

When the solar spectrum is studied carefully, we find that it is crossed by many vertical dark lines (see Spectrum Chart). These lines are called **Fraunhofer lines** and are caused by the presence in the outer layer of the sun's atmosphere of many gaseous elements which absorb certain characteristic portions of the light. The same effect may be observed in the laboratory if a beam of white light is passed through a sodium flame and then into a spectroscope; a dark line will be seen which is in the same place in the spectrum as the usual *D* line of the sodium spectrum.

SUMMARY OF CHAPTER XXV

ALL SODIUM, POTASSIUM, AND AMMONIUM SALTS are at least moderately soluble in water. Sodium, potassium, and ammonium ions are positive and monovalent.

THE CHLORIDES of sodium and potassium occur in nature and are used to prepare other compounds of these metals.

THE HYDROXIDES of these two metals are prepared by the electrolysis of the chloride solutions, or by the action of lime on the carbonate. They are strong bases.

THE CARBONATES occur in plant ashes. They are manufactured by the *Leblanc process*. Sodium carbonate is manufactured by the *Solvay process;* this consists in the action of carbon dioxide on the ammoniacal solutions of the chlorides, which forms the bicarbonate. The carbonate is made from the bicarbonate by heating.

THE CARBONATES ARE USED in washing powders and in making glass and other compounds. *Sodium bicarbonate* is one component of baking powders and is also used in chemical fire extinguishers.

SOLUTIONS OF THE CARBONATE are weakly alkaline, because of the excess of hydroxyl ions left by the formation of undissociated carbonic acid from the hydrogen ions of water. This action is called *hydrolysis.*

HYDROLYSIS is the action of the ions of water on dissolved salts. Salts formed by a weak acid and a strong base give *alkaline* reactions. Salts formed by a strong acid and a weak base give *acid* reactions.

POTASSIUM COMPOUNDS are essential for the growth of land plants and are therefore used as fertilizers. The chief source is the Stassfurt deposits in Germany.

METALLIC SODIUM AND POTASSIUM are made by the electrolysis of the fused hydroxides. They are very active substances. Metallic sodium is used to prepare *sodium peroxide*, an active oxidizing agent.

AMMONIUM compounds resemble potassium compounds in many respects.

SODIUM compounds color a Bunsen flame *yellow;* potassium compounds color the flame *purple.*

THE SPECTROSCOPE enables one to detect extremely small quantities of sodium, potassium, etc., by analyzing the light from the flame into characteristic colored lines.

QUESTIONS

1. What properties have ammonium salts in common with those of sodium and potassium?

2. Why is caustic soda cheaper than caustic potash?

3. Why are baking powders used in cooking?

4. What ingredient is common to all baking powders?

5. Explain why the water solution of sodium carbonate gives an alkaline reaction with litmus.

6. Describe three sources of common salt.

7. How would you prepare chemically pure (C. P.) sodium chloride from salt?

8. What are the most important uses of the two carbonates of sodium?

9. How could you distinguish in the laboratory between sodium carbonate and bicarbonate?

10. How would you test a compound for potassium in the presence of sodium?

11. Explain why a given weight of sodium hydroxide " goes farther " in neutralizing an acid than the same weight of potassium hydroxide.

12. Why is metallic sodium not prepared by the electrolysis of sodium chloride?

13. When a Seidlitz powder is dissolved in water there is much effervescence. Explain.

(Seidlitz powder contains tartaric acid in white paper and sodium bicarbonate and Rochelle salt in blue paper.)

14. What would happen in Question 13 if the patient took the contents of the papers *separately?* Don't try it!

15. Compare the solubility curves of sodium chloride and potassium nitrate. What practical use is made of this difference in solubility of these two salts?

16. What takes the place of baking powder in making "raised bread"?

17. Write the necessary equations to show the reactions involved in changing sodium chloride into sodium bicarbonate; sodium chloride into metallic sodium; sodium bicarbonate into sodium sulfate.

18. Write equations for the preparation of sodium hydroxide by three different methods.

TOPICS FOR FURTHER STUDY

Common salt. Why is salt said to be one of the foundation stones of all chemical industry? What is its direct connection with human life? What two substances which are made from it are found in every household? What is the cheapest source of salt? (*Martin's* Modern Chemistry.)

The chemistry of the stars. How has the spectroscope enabled astronomers to tell what chemical elements are present in the stars? What is the probable origin of the solar system? (*Duncan's* Some Chemical Problems of To-day and *J. C. Philip's* Romance of Modern Chemistry.)

CHAPTER XXVI

THE HALOGENS

Chlorine — preparation, properties, uses. Bromine — occurrence, preparation, properties — hydrobromic acid — bromides. Iodine — hydriodic acid — iodides. Replacement of halogens. Fluorine — hydrofluoric acid. Comparison of the halogens.

312. The halogens. We have already met the element chlorine a number of times in such compounds as hydrochloric acid and common salt. There are three other elements — fluorine, bromine, and iodine — which resemble chlorine in many respects and which together with chlorine are called the **halogens.** This family of elements is characterized by the fact that all the members are nonmetals with the valence of one. They form monovalent negative ions which are known as the chloride ion, fluoride ion, bromide ion, and iodide ion respectively. These ions are derived from the corresponding acids, which are water solutions of gaseous compounds containing one atom of hydrogen and one of the nonmetal.

CHLORINE

This element is very widely distributed in the form of chlorides. We have already considered the most important, namely, those of sodium and potassium. Sodium chloride is the source of all chlorine compounds.

313. Preparation. Industrially chlorine is prepared as a by-product in the manufacture of sodium hydroxide (§ 295). The gas which is evolved during the electrolysis of sodium chloride is usually very pure and is either used directly or is compressed and liquefied for transportation. Large quantities of it are converted into an important compound called bleaching powder, which will be described in the next chapter.

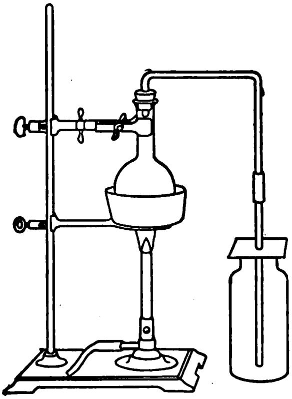


Fig. 188. Laboratory preparation of chlorine.

In the laboratory chlorine is prepared from concentrated hydrochloric acid (Fig. 188). This acid is treated with an oxidizing agent which oxidizes the hydrogen of the acid to water and sets chlorine free. Manganese dioxide (MnO_2) is commonly employed as the oxidizing agent. The reaction is as follows:

$$4\,HCl + MnO_2 \longrightarrow MnCl_2 + 2\,H_2O + Cl_2\uparrow$$

Instead of employing hydrochloric acid it is possible to use a mixture of sodium chloride and sulfuric acid, which produces hydrochloric acid:

$$MnO_2 + 2NaCl + 2H_2SO_4 \longrightarrow MnSO_4 + Na_2SO_4 + 2H_2O + Cl_2\uparrow$$

314. Properties. Chlorine is a greenish yellow gas with a very irritating odor. It is extremely poisonous and exposure even for short periods to a low concentration of it will produce serious lung trouble. For this reason it was the first "poison gas" used in the World War. A so-called "cloud attack" with this gas is shown in figure 189. It is about two and a half times as heavy as air. It can very readily be liquefied at ordinary temperatures by applying a pressure of between six and seven atmospheres. Liquid chlorine is now an article of commerce and is sold in strong steel cylinders.

315. Chemical activity. Chlorine is an extraordinarily active substance. It combines with a number of elements at room temperature, forming the chlorides with the evolution of much heat. Powdered antimony and arsenic burst into flame when they are introduced into the gas. A jet of hydrogen if lighted in the air will continue to burn in an atmosphere of chlorine (Fig. 190). This combustion is unusual inasmuch as no oxygen is involved. The reaction which takes place and which produces heat and light is the combination of hydrogen and chlorine to form hydrogen chloride. The white fumes of hydrochloric acid can be seen if one breathes into the jar. Many compounds of carbon and hydrogen — for example, turpentine — react so vigorously with chlorine that a flame is produced. The other products of the reaction are free carbon and hydrochloric acid.

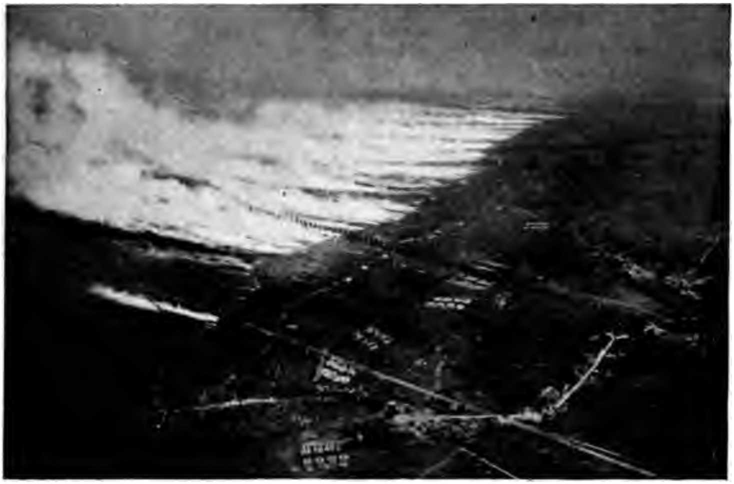


Fig. 189. Cloud attack with chlorine during the World War.

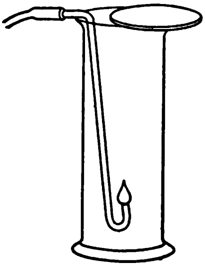


Fig. 190. Burning hydrogen in chlorine.

316. Chlorine water. Chlorine is somewhat soluble in water: one volume of water under ordinary conditions dissolves about three volumes of the gas. The chlorine is partly in true solution and partly present as two compounds, hydrochloric acid and hypochlorous acid. This latter substance is unstable and breaks down easily into oxygen. Industrially it is a very valuable substance because of its oxidizing power.

317. Uses. Chlorine is very extensively used in the industries (see Industrial Chart on page 205). It enters into the manufacture of certain other chlorine compounds, such as sulfur chloride, carbon tetrachloride, and chloroform. Its main use lies in the production of dilute solutions of hypochlorous acid or the salts of this acid, both of which are important as bleaching and disinfecting agents (Chapter XXVII).

BROMINE

Bromine occurs as the bromides of sodium and magnesium in certain deposits of common salt. The bromides can be extracted and separated from the chlorides by crystallization, or the bromine can be freed directly and then converted into any desired bromine compounds.

318. Preparation. Bromine can be prepared in much the same way as chlorine; that is, either by electrolysis of a solution of sodium bromide or by the oxidation of hydrobromic acid. If a mixture of sodium bromide and sodium chloride is electrolyzed, bromine is given off at the positive electrode before the chlorine. Advantage is taken of this fact in obtaining free bromine from the salt deposits just mentioned.

In the laboratory we employ a mixture of manganese dioxide, sodium bromide, and sulfuric acid, which is equivalent to hydrobromic acid. The equation is similar to that for making chlorine.

$$2NaBr + MnO_2 + 2H_2SO_4 \longrightarrow Na_2SO_4 + MnSO_4 + 2\,H_2O + Br_2$$

The laboratory preparation of bromine is usually carried out in an apparatus called a retort (Fig. 191). The mixture of sodium bromide, sulfuric acid, and manganese dioxide is placed in the retort and gently heated. Bromine vapors fill the retort and condense in a cool receiver which is provided. Since bromine does not mix with water it is convenient to place some water in the receiver. A layer of bromine then collects under this water, and the fumes do not escape into the atmosphere.

319. Properties. Bromine is a dark, brownish red liquid, about three times as heavy as water; it is the only nonmetallic element which is a liquid under ordinary conditions. It has a strong, suffocating smell (the name bromine means a *stench*) and attacks the nose and throat, as chlorine does, and irritates the eyes. The liquid produces very painful burns on the skin, and great care should be taken in handling it. It is somewhat soluble in water, and such a solution is commonly called **bromine water.** Like the aqueous solution of chlorine, it is an oxidizing agent.

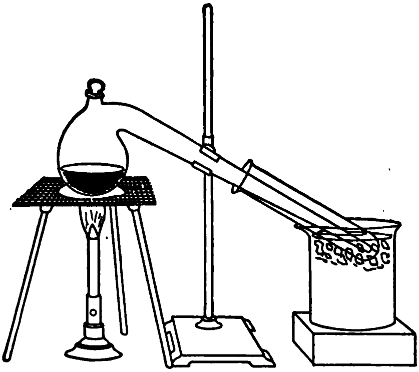


Fig. 191. Laboratory preparation of bromine.

Bromine is not quite so active as chlorine but combines readily with a number of elements with the evolution of much heat and light.

320. Hydrogen bromide. Hydrogen bromide is a gaseous substance similar in many ways to hydrogen chloride. It cannot, however, be satisfactorily prepared by the same reaction. When we heat sodium bromide and concentrated sulfuric acid, we produce hydrogen bromide, but this substance is so readily oxidized by the warm concentrated sulfuric acid that part of it becomes water and free bromine:

$$\mathrm{NaBr + H_2SO_4 \longrightarrow NaHSO_4 + HBr}$$

$$\mathrm{2\,HBr + H_2SO_4 \longrightarrow 2\,H_2O + SO_2\uparrow + Br_2\uparrow}$$

For this reason we use some other method when we wish to prepare hydrogen bromide. One way is to treat a mixture of red phosphorus and water with bromine. Red phosphorus and bromine combine to form the compound phosphorus tribromide (PBr_3). This compound immediately reacts with the water, forming pure hydrogen bromide and phosphorous acid (H_3PO_3), which is not volatile:

$$PBr_3 + 3\ H_2O \longrightarrow 3\ HBr + H_3PO_3$$

Hydrogen bromide is a colorless gas, very soluble in water; its aqueous solution is known as **hydrobromic acid.** Hydrobromic acid is a strong acid. It is much more easily oxidized to water and the free element than is hydrochloric acid.

321. Bromides. The salts which are formed by neutralizing hydrobromic acid are called **bromides.** *All bromides are soluble except those of silver, lead, and mercury.* Silver bromide is a yellowish solid, used extensively in photography. The bromides of sodium and potassium are valuable as drugs.

IODINE

Iodine in the form of iodides occurs to a small extent in certain salt deposits. It is also found in the deposits of sodium nitrate in Chile. This is the principal source of the element, although it is also sometimes prepared from the ash obtained by burning certain seaweeds.

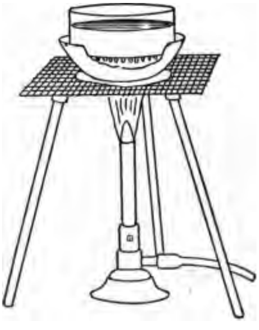


Fig. 192. Laboratory preparation of iodine.

322. Preparation and properties. Iodine is prepared in exactly the same way as bromine and chlorine.

The preparation of iodine can be conveniently carried out by warming a mixture of manganese dioxide, sulfuric acid, and sodium iodide in an evaporating dish on top of which is placed a dish containing cold water. The iodine vaporizes and condenses on the under side of the top dish, forming a mass of beautiful crystals *(Fig. 192).*

Iodine is a steel-gray solid which is very easily vaporized. The vapor has a beautiful violet color and on being cooled passes back directly into a solid. This process of passing from solid to vapor and back again without the formation of a liquid is called **sublimation.** Iodine is only slightly soluble in water but is quite soluble in a solution of sodium or potassium iodides. It is also soluble in alcohol and is commonly sold in such a solution as **tincture of iodine.**

Iodine is less active than either of the other two halogens that we have considered; however, it will combine directly with many nonmetals at room temperature or when slightly warmed.

A very characteristic reaction of iodine is the formation of a blue color when a small amount is brought into contact with starch. *This reaction is employed as a test for either iodine or starch.*

323. Hydrogen iodide. Hydrogen iodide cannot be prepared by heating sodium iodide and sulfuric acid, for the same reason that this general method was impossible with hydrobromic acid. It is produced by the interaction of red phosphorus, iodine, and water. Hydrogen iodide readily dissolves in water and forms the solution called **hydriodic acid.** This acid is even more easily oxidized than hydrobromic acid and is therefore a good reducing agent. It is a strong acid and on neutralization forms salts called **iodides.**

324. Iodides. *All iodides except those of silver, lead, and mercury are soluble compounds.* Silver iodide is a yellow, insoluble substance, and like silver bromide is used in photography. Certain iodides are necessary in the preparation of drugs; iodine itself is used in medicine.

325. The replacement of halogens. If we pass chlorine into a solution of a bromide or an iodide, we find that free bromine or iodine respectively is liberated and a chloride formed. This is a replacement reaction and is like the reaction in which metallic zinc liberated hydrogen from the hydrogen ion, except that we are now dealing with negative ions:

$$\mathrm{Cl_2 + 2\,Br^- \longrightarrow 2\,Cl^- + Br_2}$$

$$\mathrm{Cl_2 + 2\,I^- \longrightarrow 2\,Cl^- + I_2}$$

Bromine will liberate iodine from the iodide; but iodine will liberate neither bromine nor chlorine from their salts. We can therefore write these three elements as a series in which the higher member will liberate any element below it from its ion.

REPLACEMENT SERIES OF NONMETALS

Chlorine
Bromine
Iodine

This table also indicates the **order of activity** of these nonmetals, that is, chlorine is most active and iodine is least.

Since chlorine is cheap and is easily obtained it is sometimes used to liberate bromine or iodine from a solution of its salts and in this way to prepare the free elements on a large scale.

FLUORINE

The fourth member of the halogen family differs somewhat from the others. This difference is more apparent than real and is due mainly to the fact that fluorine *is itself far more active than the other halogens and that its compounds are much more stable.* Fluorine occurs as a constituent of one or two important minerals, of which fluorite (CaF_2) and cryolite (Na_3AlF_6) may be mentioned. The former is used as the chief source of fluorine and its compounds. Fluorine compounds are somewhat poisonous and are used in large amounts in the manufacture of insect powders.

326. Preparation and properties. Fluorine is a slightly yellow gas, extremely poisonous and corrosive, and is very difficult to liquefy. It is the most active element known and at ordinary temperatures combines vigorously with most of the elements. Fluorine can be prepared only with difficulty. A French chemist, Moisson, in 1886 first isolated it by the *electrolysis* of a solution of potassium fluoride (KF) in liquid hydrogen fluoride (H_2F_2). The experiment had to be performed in platinum or copper apparatus as all other materials were attacked by the gas.

327. Hydrogen fluoride. Hydrogen fluoride can be prepared by the action of concentrated sulfuric acid on calcium fluoride:

$$CaF_2 + H_2SO_4 \longrightarrow CaSO_4 + H_2F_2$$

It is a gas which is very soluble in water, forming an acid called **hydrofluoric acid**. Hydrogen fluoride is much more stable than hydrogen chloride and cannot be oxidized at all. It is easily condensed to a liquid, which boils at 19° C.

Hydrofluoric acid is a strong acid and forms salts called fluorides. It is noteworthy because it will dissolve a great many substances, including sand (SiO_2) and glass. For this reason it is kept in wax bottles. Its action with sand results in the formation of the gas **silicon tetrafluoride** (SiF_4) and water:

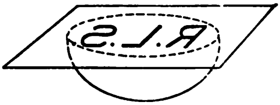


Fig. 193. Etching glass with hydrofluoric acid.

$$SiO_2 + 2\ H_2F_2 \longrightarrow SiF_4 + 2\ H_2O$$

The action with glass takes place in much the same way since glass is a compound of silicon. This action of hydrofluoric acid on glass is taken advantage of in etching designs on that material. The glass is painted over with wax except where it is desired to have it etched, and hydrofluoric acid is applied (Fig. 193). After a time the acid is washed off and the wax removed; the glass is opaque where the acid has come in contact with it.

328. Comparison of the halogens. The following table summarizes the important physical and chemical properties of the halogen family, the elements being arranged in the order of their atomic weights. It should be remembered that the activity of these elements decreases progressively from fluorine to iodine, and that the stability of the hydrogen compounds decreases in the same order. This is also the order in which they replace each other. Fluorine is so active that it replaces the oxygen of water. Because of this extreme activity it is to be regarded somewhat in the light of an odd member of the series; although its behavior seems more normal when we realize that it stands above chlorine in the family, and hence should be more active than even this active element.

NAME	ATOMIC WEIGHT	BOILING POINT	STATE	COLOR
Fluorine (F)	19.0	– 187° C.	gas	pale yellow
Chlorine (Cl)	35.5	– 33.6°	gas	greenish yellow
Bromine (Br)	79.9	63°	liquid	red
Iodine (I)	126.9	184.4°	solid	purplish black

SUMMARY OF CHAPTER XXVI

FLUORINE, CHLORINE, BROMINE, AND IODINE are all monovalent, nonmetallic elements and are called the ***halogens.***

CHLORINE is prepared industrially by the electrolysis of sodium chloride. It is prepared in the laboratory by the oxidation of hydrochloric acid with manganese dioxide.

Chlorine is a very active element and combines with many elements at room temperature. It is somewhat soluble in water, and its water solution contains hypochlorous acid, which is an oxidizing agent. Chlorine is used for preparing solutions of this acid and of its salts. The salts are used extensively in the industries.

BROMINE is prepared from a bromide by heating with manganese dioxide and concentrated sulfuric acid. It is a liquid. It is somewhat less active than chlorine.

Hydrobromic acid is not made by the action of sulfuric acid on a bromide, but is best prepared by adding water to phosphorus tribromide.

IODINE is prepared from an iodide by heating with manganese dioxide and concentrated sulfuric acid. It is a solid which sublimes on heating.

Hydriodic acid is a good reducing agent. It cannot be prepared from an iodide with sulfuric acid.

FLUORINE is an extremely active element. It is prepared by electrolysis in a special apparatus. Hydrofluoric acid is made by heating calcium fluoride with sulfuric acid. It will dissolve sand and glass.

***Chlorine will replace bromine and iodine* from their salts; *bromine will replace iodine;* fluorine is so active that it replaces the oxygen from water.**

QUESTIONS AND PROBLEMS

1. What properties have all the halogens in common?

2. How could you distinguish bromine vapor from nitrogen dioxide?

3. How could you identify a chloride, a bromide, and an iodide?

4. Write the equations for the reaction of chlorine with hydrogen; with zinc; and with antimony.

5. How do you account for the smell of hydrogen sulfide which is produced when concentrated sulfuric acid is added to an iodide?

6. How would you test for free iodine?

7. What precautions must be taken in handling hydrofluoric acid?

8. How would you prove the presence of starch in beans?

9. How many kilograms of sodium chloride would be required to prepare 2 liters of chlorine gas at 20° C. and under a pressure of 5 atmospheres?

10. Calculate the per cent of fluorine in fluorspar (CaF_2).

11. How would you separate a mixture of iron and iodine?

12. A compound contains 2.1% hydrogen, 12.8% carbon, and 85.1% bromine. At 140° C. and 76 cm., 1.00 gram of its vapor occupies 180 cc. Calculate its formula.

TOPIC FOR FURTHER STUDY

Poison gas in the World War. What gas was first used in the war? When and where was the attack made? What other gases were subsequently used? In what form? (*Slosson's* Creative Chemistry and *Auld's* Gas and Flame.)

CHAPTER XXVII

HYPOCHLOROUS ACID AND OTHER OXIDIZING SUBSTANCES

Hypochlorous acid — properties — oxidizing action — chlorine water — hypochlorites — bleaching — disinfecting and antiseptic action. Hydrogen peroxide, preparation and properties — peroxides — ozone.

329. Oxidizing substances. The most important use of chlorine is in the preparation of dilute solutions of hypochlorous acid ($HOCl$) and its salts. These substances are of the greatest value because they are cheap and efficient oxidizing agents in aqueous solutions and serve as **bleaching agents** and **antiseptics.** In this chapter we shall learn how hypochlorous acid and some other oxidizing agents, such as hydrogen peroxide and ozone, may be prepared and used.

330. Hypochlorous acid ($HOCl$). Chlorine water contains, besides the dissolved chlorine, some hydrochloric acid and hypochlorous acid. The reaction between water and chlorine which forms these two acids is reversible:

$$Cl_2 + H_2O \rightleftharpoons HCl + HOCl$$

In order to prepare a solution of pure hypochlorous acid, we treat chlorine water with some substance which will use up the hydrochloric acid and leave no other impurities in its place. This can be done by shaking chlorine water with silver carbonate (Ag_2CO_3), a substance which is practically insoluble in water. This reacts with the hydrochloric acid, forming water, silver chloride, and carbon dioxide. The silver chloride is insoluble, and this reaction runs to completion; and therefore, also, the reaction between chlorine and water. Hypochlorous acid is a very weak acid and hence does not react with the silver carbonate. We thus end with a dilute solution of hypochlorous acid containing silver chloride in suspension. The silver chloride can be filtered off.

$$2\ HCl + Ag_2CO_3 \longrightarrow 2\ AgCl + H_2O + CO_2 \uparrow$$

$$2\ Cl_2 + 2\ H_2O + Ag_2CO_3 \longrightarrow 2\ HOCl + 2\ AgCl \downarrow + H_2O + CO_2 \uparrow$$

331. Properties. Hypochlorous acid is known only in solution. The dilute solution prepared in the way just described shows the properties of a weak acid. *It is an extremely unstable substance* and tends to decompose, forming hydrochloric acid and oxygen according to the following equation:

$$2\ HOCl \longrightarrow 2\ HCl + O_2$$

Because of this instability hypochlorous acid cannot exist in concentrated solutions.

332. Oxidizing action. Because hypochlorous acid so readily loses its oxygen, it is a powerful oxidizing agent even in a dilute solution. For example, it rapidly oxidizes sulfurous acid to sulfuric acid:

$$H_2SO_3 + HOCl \longrightarrow H_2SO_4 + HCl$$

It will also oxidize many complicated organic compounds. It will oxidize hydrogen sulfide to water and free sulfur:

$$H_2S + HOCl \longrightarrow H_2O + HCl + S \downarrow$$

333. Chlorine water. Pure dilute hypochlorous acid is rather expensive to prepare. For almost any purpose chlorine water will serve equally well since the presence of hydrochloric acid in the solution does no harm. As fast as the hypochlorous acid is used up by a reducing agent, more of the dissolved chlorine reacts with the water and produces additional hypochlorous acid, until finally all the dissolved chlorine has been used up and converted into hydrochloric acid.

The slow decomposition of hypochlorous acid with the formation of free oxygen can be shown by filling a tube with chlorine water and allowing it to stand in the sunlight. A gas which can be shown to be oxygen collects in the top of the tube (Fig. 194):

$$2\ Cl_2 + 2\ H_2O \longrightarrow 4\ HCl + O_2$$

The oxidizing action of chlorine water can be demonstrated by treating a solution of sulfur dioxide with chlorine water. The sulfurous acid solution before such treatment will not give a precipitate with barium chloride in the presence of hydrochloric acid; but after it has been oxidized with the chlorine water a heavy precipitate is formed, showing the presence of sulfuric acid:

$$Cl_2 + H_2O + H_2SO_3 \longrightarrow H_2SO_4 + 2\ HCl$$

A solution of hydrogen sulfide in water forms a precipitate of sulfur on being treated with chlorine water, indicating that the oxidation has taken place:

$$Cl_2 + H_2O + H_2S \longrightarrow H_2O + 2\ HCl + S \downarrow$$

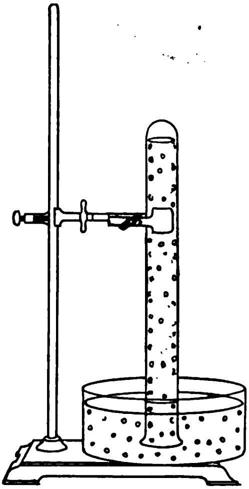


Fig. 194. Chlorine water decomposes in sunlight.

334. Hypochlorites. The salts of hypochlorous acid are called **hypochlorites.** They can be prepared by neutralizing hypochlorous acid, but they are more conveniently produced by other methods.

Sodium hypochlorite (NaOCl) is formed when chlorine is run into a *cold dilute* solution of sodium hydroxide:

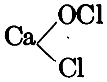
$$Cl_2 + 2\ NaOH \longrightarrow NaOCl + NaCl + H_2O$$

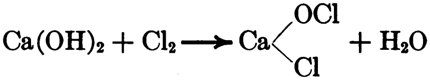
What really happens in this case is that the sodium hydroxide neutralizes both the hypochlorous acid and the hydrochloric acid, which are in equilibrium with chlorine and water. Sodium hypochlorite can also be prepared by electrolyzing a solution of sodium chloride in a single narrow cell without a diaphragm. Chlorine is liberated at one pole, and sodium hydroxide is formed at the other. The two substances come in contact and form sodium hypochlorite. In both these methods for the preparation of sodium hypochlorites it will be noted that a dilute solution of the hypochlorite is formed which contains considerable sodium chloride, but the presence of this latter substance does not interfere with the usefulness of the hypochlorite.

The hypochlorites are unstable substances. On account of this instability they are always prepared and used in cold dilute solutions. On being warmed or on long standing they oxidize themselves into compounds containing more oxygen, called **chlorates**. Sodium hypochlorite solution, for example, on heating gives sodium chloride and **sodium chlorate** ($NaClO_3$):

$$3\ NaOCl \longrightarrow 2\ NaCl + NaClO_3$$

Potassium chlorate we have already used; it is made by the action of chlorine on *warm* potassium hydroxide.

335. Bleaching powder ($CaCl(OCl)$). This substance is made by the action of chlorine on slaked lime. It is a white powder which is rather unstable and smells strongly of hypochlorous acid. Pure calcium hypochlorite would have the formula $Ca(OCl)_2$. Bleaching powder acts very much like a **mixed salt** of calcium chloride and calcium hypochlorite, and has the formula  $Ca\langle{}^{OCl}_{Cl}$ or $CaCl(OCl)$:



$$Ca(OH)_2 + Cl_2 \longrightarrow Ca\langle{}^{OCl}_{Cl} + H_2O$$

Bleaching powder, or "**chloride of lime**," serves as a commercial source of hypochlorous acid since lime is a cheap base. (See Industrial Chart on page 205.)

336. Bleaching. Hypochlorous acid is a powerful bleaching agent; this is the most important use to which it and its salts are put. Most coloring materials are complicated organic substances which can be oxidized into colorless compounds. The oxidation is very readily accomplished by a dilute solution of hypochlorous acid, which sets free **nascent oxygen**:

$$HOCl \longrightarrow HCl + [O]$$

This action can easily be shown by dipping a piece of colored cloth in chlorine water or by suspending a piece of moistened cloth in an atmosphere of chlorine (Fig. 195). *Dry chlorine has no oxidizing action,* for it cannot form hypochlorous acid.

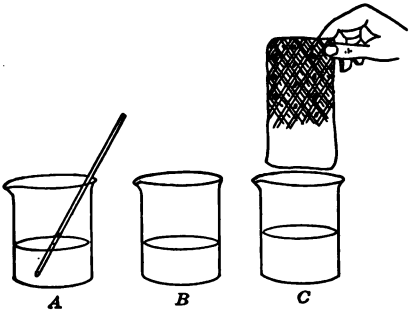


Fig. 195. Bleaching colored cloth.
A, dil. H_2SO_4; *B*, sol. of bleaching powder; *C*, H_2O.

Bleaching is a very important process in a great number of industries. For example, most fabrics, such as cotton cloth, are colored slightly yellow by natural impurities and must be bleached before they can be put on the market. Figure 196 shows the general scheme for bleaching cloth. The cloth passes through alternate vats of bleach (*B*) solution and very dilute sulfuric acid (*S*). In this way the hypochlorous acid is produced only within the fibers of the cloth, where it will be most effective. Then it goes through a solution of sodium sulfite (*C*) to destroy any remaining hypochlorous acid which might weaken it. Finally the cloth is washed in water (*W*) and ironed by passing over hot rolls (*H*).

Bleaching with hypochlorous acid is generally carried out in industrial works in one of the following ways: (1) chlorine water is prepared by running chlorine gas into cold water, and this solution is used directly; (2) sodium hypochlorite prepared by electrolysis or from chlorine gas and an alkali is used; (3) a suspension of bleaching powder in water is used. This latter method is the one commonly employed in the household. Fabrics must be thoroughly washed after being bleached in order to remove the chemicals, which would otherwise slowly rot the cloth.

Since hypochlorous acid is very weak it is easily displaced from its salts by other acids. When a hypochlorite is treated with dilute acid, a solution of hypochlorous acid results, which can then act as a bleaching agent. In the commercial use of the hypochlorites this is accomplished, as described above, by treating the material to be bleached first with the hypochlorite and then with dilute acid. When " bleaching powder " is used in the household, the acid required is slowly supplied by carbon dioxide in the air. The equations are:

$$CaCl(OCl) + CO_2 + H_2O \longrightarrow CaCO_3 + HOCl + HCl$$

$$HOCl \longrightarrow HCl + [O] \text{ used up in the bleaching.}$$

337. Disinfecting and antiseptic action. Diseases are caused and communicated by certain minute plants called **bacteria.** These microörganisms are generally present where there is much waste organic material. Hypochlorites readily oxidize such organic material and destroy the bacteria. For this reason " chloride of lime " has long been used in the household as a disinfectant. More recently a solution of sodium hypochlorite (prepared by the electrolysis of salt solution) has come into use for washing the floors and walls in hospitals and sick rooms.

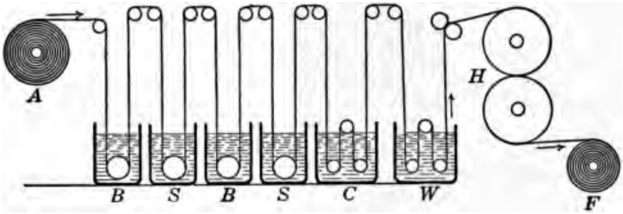


Fig. 196. Diagram of the commercial process of bleaching.

Hypochlorous acid has recently been used as an **antiseptic agent** in surgery. Because of the sensitiveness of flesh to chemical reagents it must be employed only in very dilute solutions and under certain special conditions. **Dakin's solution**, which has been found most valuable in dressing wounds, is essentially a solution of sodium hypochlorite, containing from 0.45 to 0.5 per cent of this substance. The solution must be made in such a way that it is practically neutral; if it were either alkaline or acid it would be too corrosive in an open wound. Furthermore, it is used most advantageously when the patient can be so arranged that a stream of the solution continually passes into the wound and washes it out.

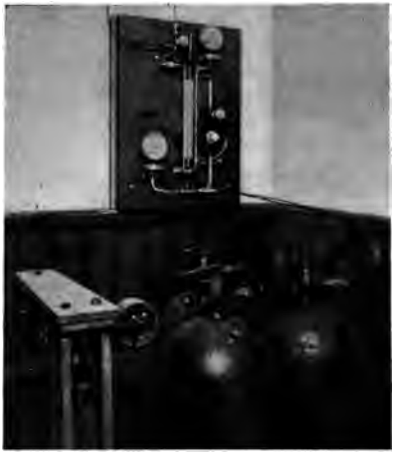


Fig. 197. Purification of water by chlorine.

The bacteria which are present in drinking water can readily be destroyed by hypochlorous acid. This is usually done by adding a small amount of a hypochlorite solution, or by running a small stream of chlorine gas from steel cylinders containing liquefied chlorine into the water supply (Fig. 197). About one part of hypochlorous acid in a million parts of water will completely purify all except the most polluted supplies. This method of purification has been adopted by many cities and towns.

338. Hydrogen peroxide (H_2O_2). Another oxidizing agent of importance is hydrogen peroxide. This substance contains one more atom of oxygen than water. It is unstable and easily decomposes, giving water and free oxygen; for this reason it is a powerful oxidizing agent.

When sodium peroxide is treated with *ice-cold dilute hydrochloric acid,* it forms hydrogen peroxide and sodium chloride:

$$Na_2O_2 + 2\,HCl \longrightarrow 2\,NaCl + H_2O_2$$

Industrially the substance is made by the action of *cold dilute* sulfuric acid on barium peroxide:

$$BaO_2 + H_2SO_4 \longrightarrow BaSO_4 + H_2O_2$$

The barium sulfate is insoluble and can be removed by filtration.

339. Properties and uses. Hydrogen peroxide can be prepared as an absolutely pure substance, but it is extremely unstable and is never used except in dilute solutions. It is commonly sold as a three per cent solution under the name of **hydrogen peroxide.** It is a vigorous oxidizing agent and will oxidize sulfurous acid to sulfuric and liberate free sulfur from hydrogen sulfide. On standing, strong solutions of it liberate oxygen:

$$2\ H_2O_2 \longrightarrow 2\ H_2O + O_2$$

It is used extensively as a disinfecting and antiseptic agent. It has certain antiseptic powers, but they are extremely small compared with other good antiseptics. But it has the valuable property of giving off free oxygen when it comes in contact with open wounds, and the mechanical action of this evolved gas serves to cleanse the wound and to remove any foreign material. For this reason hydrogen peroxide is valuable in cleaning old wounds and in removing gauze and bandages.

340. Peroxides. The atoms in hydrogen peroxide are probably linked in the following manner: H—O—O—H. The peroxides are substances which have two oxygen atoms linked in this way; when treated with acids they form hydrogen peroxide. Like hydrogen peroxide they are strong oxidizing agents in aqueous solution. Sodium peroxide, when treated with water at ordinary temperatures, forms oxygen and is sometimes used for preparing this element:

$$2\ Na_2O_2 + 2\ H_2O \longrightarrow 4\ NaOH + O_2$$

341. Ozone (O_3). When oxygen is exposed to a silent discharge from an induction coil, it partially changes into an allotropic form called **ozone.** This substance has three atoms to the molecule; its formation from oxygen is reversible, and the equation is as follows:

$$3\ O_2 \rightleftharpoons 2\ O_3$$

At the maximum only about 7 per cent of oxygen can be converted into ozone (Fig. 198). Its formation from oxygen involves an absorption of energy; conversely, when it passes back into oxygen, it gives out energy. In general, allotropic forms of elements have different energy contents, and the unstable form tends to pass into the more stable with the evolution of energy.

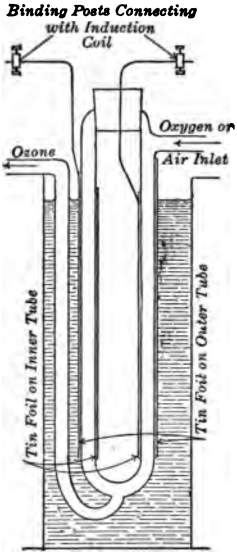


Fig. 198. Ozone generator.

Ozone reverts to oxygen slowly at ordinary temperatures and rapidly at higher temperatures. It is a vigorous oxidizing agent and will instantly oxidize sulfur dioxide to sulfur trioxide at room temperature:

$$SO_2 + O_3 \longrightarrow SO_3 + O_2$$

It will also oxidize many organic compounds, and for this reason it is a bleaching agent. Air containing 4 or 5 per cent of ozone (prepared by an electric discharge) has been used in some places for disinfecting the water supply. It seems to act in a very satisfactory manner. It has been suggested as a means of purifying air in houses and large halls, but has not given very successful results: it is a deodorizer but has very slight disinfecting action in the air.

SUMMARY OF CHAPTER XXVII

CHLORINE WATER contains dissolved chlorine and hydrochloric and hypochlorous acids.

Pure dilute *hypochlorous acid* can be made by shaking chlorine water with silver carbonate. Hypochlorous acid is known only in solution; it is unstable, breaking down into hydrochloric acid *and oxygen.* It is a powerful oxidizing agent.

SODIUM HYPOCHLORITE is made by passing chlorine into cold sodium hydroxide or by electrolyzing sodium chloride. Sodium hypochlorite when warmed produces sodium chlorate.

BLEACHING POWDER, or *chloride of lime*, is made by the action of chlorine on slaked lime. It acts like a mixed salt ($CaCl(OCl)$).

THE HYPOCHLORITES AND HYPOCHLOROUS ACID are excellent *bleaching* agents and are used as such in the industries.

Hypochlorous acid is a *disinfecting* and *antiseptic agent* and is used in purifying drinking water. Chloride of lime is used as a disinfecting agent. *Dakin's solution* is one of the successful modern antiseptics which depend on hypochlorous acid for their action.

HYDROGEN PEROXIDE is made by treating sodium peroxide or barium peroxide with cold dilute acid. It is an unstable substance and a powerful oxidizing agent. It is sold in a three per cent solution. Its antiseptic action is slight, but it is used for cleaning wounds.

OZONE is an allotropic form of oxygen produced by the action of a silent electric discharge. It is unstable and is a powerful oxidizing agent. It is used in some places for purifying the water supply.

QUESTIONS

1. Explain how chlorine is indirectly used in bleaching cotton cloth.

2. Why is the bleaching of organic coloring matter considered a process of oxidation?

3. Why does not dry chlorine act as a bleaching agent?

4. What is the difference between hydrochloric acid and hypochlorous acid? How would you test for each?

5. What materials are injured by hypochlorous acid?

6. Explain how chlorine reacts with water to produce *nascent oxygen.*

7. What experiment could you perform in order to prove that hypochlorous acid is a weak acid?

8. Why must chlorine water always be freshly prepared?

9. If bleaching is an oxidizing action, why is free oxygen not used?

10. What advantages has hydrogen peroxide over other oxidizing agents?

11. What is the difference between oxygen and ozone?

12. Explain how hydrogen peroxide produces "nascent oxygen."

13. Show how oxygen and ozone illustrate exothermic and endothermic reactions.

14. Show how water and hydrogen peroxide illustrate the Law of Multiple Proportions.

15. Why should bottles for hydrogen peroxide be made of brown glass?

16. In what experiments have we used manganese dioxide as an oxidizing agent?

17. Compare sulfurous and hypochlorous acids as bleaching agents.

18. What is the difference between a disinfecting and an antiseptic agent?

19. How would you prepare potassium chlorate from potassium hydroxide?

20. How would you prepare "chloride of lime"? For what is it used?

CHAPTER XXVIII

THE NITROGEN FAMILY AND THE PERIODIC SYSTEM

Phosphorus, its preparation and properties — matches — phosphoric acid — phosphates as fertilizers. Arsenic and antimony. Bismuth. Useful alloys.

The Periodic System — valence — metals and nonmetals — value and use of the periodic system.

342. Family characteristics. We have already studied two **families** of elements, the alkali metals and the halogens. Now we shall consider the **nitrogen family**, which includes (besides nitrogen) phosphorus, arsenic, antimony, and bismuth. We shall observe that there are greater differences between its members than between those in the other two families. These differences are, however, gradual modifications which vary progressively as the atomic weights increase. Finally, to understand these relationships between the elements concerned, we shall presently briefly outline the periodic system. In Chapters VIII, XIX, and XX we studied nitrogen and some of its compounds; now we shall consider the rest of the group.

Phosphorus

343. History and occurrence. This element was discovered in the middle of the seventeenth century by an old philosopher (alchemist) named Brandt, who was searching for some substance which would change everything into gold. But it was not until 1833, when matches began to be manufactured, that phosphorus became at all common or cheap.

The element is found in nature in the form of phosphates. Bones and teeth contain a large amount of calcium phosphate ($Ca_3(PO_4)_2$), which gives to them their necessary hardness and rigidity. The muscles, nerves, and brains of animals contain very complex organic compounds of phosphorus. These are formed in the body from the phosphorus compounds which are contained in almost all vegetable food. The plants in turn need soluble phosphates in the soil for their growth.

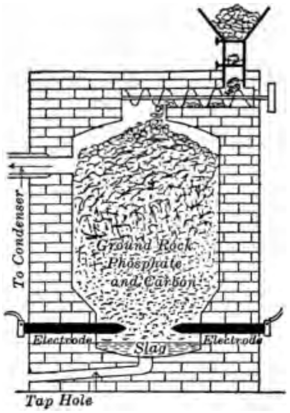


Fig. 199. Electric furnace used to prepare phosphorus.

344. Preparation. Phosphorus is obtained from the mineral calcium phosphate, which is mixed with coke and sand (SiO_2) and heated in a suitable electric furnace (Fig. 199).

We may regard calcium phosphate ($Ca_3(PO_4)_2$) as composed of two oxides, 3 CaO and P_2O_5. The calcium oxide seems to unite with the sand to form calcium silicate, which fuses to a slag and is drawn off at the bottom:

$$CaO + SiO_2 \longrightarrow CaSiO_3$$

The phosphoric anhydride (P_2O_5) is reduced by the carbon as follows:

$$2\,P_2O_5 + 10\,C \longrightarrow P_4\uparrow + 10\,CO\uparrow$$

These gaseous products pass off through a pipe, and the phosphorus is condensed under water. After further purification it is cast into sticks.

The electric arc between the electrodes of the furnace supplies the necessary heat. This heat is due to the resistance offered to the electric current, and since the heat is developed in a very restricted area, it is possible to get the high temperatures needed for this process.

345. Properties. When prepared in this way phosphorus is a white, waxy-looking solid which melts at 44° C. and boils at 287° C. Its most striking property is the low temperature *at which it* catches fire (35° C.). This necessitates its being kept under water and cut under water, for even the friction of the knife is enough to ignite it. Great care must be taken in handling it (never with the fingers) because the burns are deep and poisonous. It is not soluble in water but dissolves readily in some other liquids, such as carbon disulfide.

When exposed in a dark room *it glows;* that is, it gives out light in spite of the fact that its temperature remains low. Usually when an object gives out light we think of it as hot, and in fact most things must be heated to 600° C. or higher before they begin to glow. It is well known that glowworms, lightning bugs, and many phosphorescent sea animals have this power of emitting light without heat. This is called **luminescence.**

346. Red phosphorus. When the **white phosphorus** is heated to about 250° C. in a vessel from which air is excluded, it changes into an allotropic form called **red phosphorus.** This substance is dull red and is somewhat heavier than the white form. It is insoluble in carbon disulfide, is not poisonous, and need not be kept under water. The red phosphorus does not melt but when heated passes directly into a vapor. This vapor shows a gram-molecular weight of about 128 grams, which corresponds to the formula P_4. If the vapor is cooled quickly the white form is produced, but this very gradually changes at ordinary temperatures into the red.

Still another allotropic form of phosphorus has recently been prepared by Bridgman. By heating white phosphorus to 200° C. and subjecting it to an enormous pressure (1200 kilograms per square centimeter), he obtained **black phosphorus,** which is still heavier than the red.

347. Matches. The easy inflammability of phosphorus has resulted in its being used in the manufacture of matches. The older process consisted in coating the end of a splint of wood with a paste containing white phosphorus, an oxidizing agent, such as lead dioxide (PbO_2), and glue. The head when dry was dipped in varnish to exclude air. Because the use of white phosphorus in the making of matches led to serious cases of poisoning among the workmen, its use in match factories is prevented in the United States by a heavy tax. A nonpoisonous compound of phosphorus known as **phosphorus sesquisulfide** (P_4S_3) is now substituted. This substance is quite as suitable as white phosphorus. When the match is struck the friction warms up the sesquisulfide and in the presence of the oxidizing agent it takes fire; the heat of this combustion ignites the wood. To make the head of the match burn more easily it is usually impregnated with paraffin.

Fig. 200. Hydraulic mining of phosphate rock in Florida.

Safety matches are tipped with a mixture of an oxidizing agent, a combustible material, such as antimony trisulfide (Sb_2S_3), and a little powdered glass to increase the friction. The side of the box in which they are contained is coated with a thin layer of red phosphorus, antimony trisulfide, and glue. When the match is rubbed sufficient heat is produced to ignite a small bit of the red phosphorus in contact with the head of the match, which then takes fire. In safety matches the most combustible material (the red phosphorus) and the oxidizing agent are separated; the match can generally be lighted only when these two constituents are rubbed together. Hence safety matches must be struck on the side of the box.

348. Phosphoric Acid. When phosphorus burns with a free supply of oxygen, a white powder is formed known as **phosphorus pentoxide** (P_2O_5):

$$4\,P + 5\,O_2 \longrightarrow 2\,P_2O_5$$

The most characteristic property of the pentoxide is its great attraction for water. Since it has no chemical effect upon most gases, the latter may be very thoroughly dried by allowing them to pass through tubes containing phosphorus pentoxide.

When this oxide is dissolved in boiling water, phosphoric acid is formed:

$$P_2O_5 + 3\,H_2O \longrightarrow 2\,H_3PO_4$$

349. Phosphates as fertilizers. Since phosphoric acid is a *tribasic* acid it can form three classes of salts, according as one, two, or three of the hydrogen atoms are replaced by a metal. The rock phosphates of Florida (Fig. 200), Georgia, Tennessee, and the Carolinas are very largely composed of calcium phosphate ($Ca_3(PO_4)_2$). Since this phosphate is almost insoluble in water it is converted by the action of sulfuric acid into the calcium dihydrogen phosphate ($Ca(H_2PO_4)_2$), which is much more soluble:

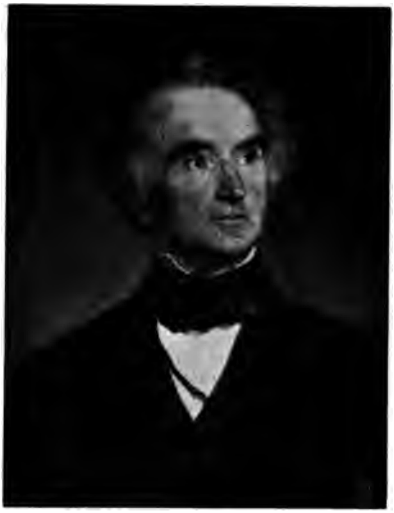


FIG. 201. JUSTUS LIEBIG (1803–1873).
German chemist who established the first student laboratory and laid the foundations of modern agricultural chemistry.

$$Ca_3(PO_4)_2 + 2\,H_2SO_4 \longrightarrow 2\,CaSO_4 + Ca(H_2PO_4)_2$$

The resulting mixture of calcium sulfate and calcium acid phosphate is known as ***superphosphate of lime**, which is a fertilizer*.

The composition and proper use of fertilizers is one of the important subjects of investigation in **agricultural chemistry**, which was founded by Liebig (Fig. 201). We have seen that in order to maintain the fertility of the soil *there must be supplied to it three substances:* (1) *nitrogen compounds,* (2) *potassium compounds,* and (3) *soluble phosphates.* Commercial fertilizers are usually a mixture of these three fundamental materials. But the composition of the fertilizer has to be varied to suit the needs of the crop to be raised and the composition of the soil. It frequently happens that soil needs **liming** because it contains too much acid formed from decomposing vegetable matter. Such crops as grains and grass will not thrive on *sour* soil, and so it is *sweetened* by spreading slaked lime ($Ca(OH)_2$) upon it.

ARSENIC AND ANTIMONY

The next two members of the family, arsenic and antimony, are of minor importance, and we shall consider them but briefly. They look very much like metals, and in their physical properties they show little resemblance to either nitrogen or phosphorus. They behave, however, essentially as nonmetals.

350. Occurrence and preparation. Both elements occur in nature as sulfides. The ore is roasted, forming an oxide, which is then reduced. Most of the natural sulfides contain more or less arsenic; when these ores are oxidized, the sulfur dioxide passes off as a gas, while the arsenic trioxide (As_2O_3) settles as a solid in the flues. The deposit is reduced with carbon:

$$As_2O_3 + 3\,C \longrightarrow 2\,As \uparrow + 3\,CO \uparrow$$

351. Properties and uses. Both elements have a silvery luster; arsenic tarnishes quickly, but antimony does not tarnish. Metallic arsenic is added in very small amounts (about 0.5 per cent) to lead in making small shot. The arsenic lowers the freezing point of the solvent lead and delays its solidification as it drops from the top of the shot tower. It also imparts to the lead the required hardness.

Finely powdered antimony, known as **antimony black,** is used to coat plaster casts in order to give them a dull metallic appearance.

When these elements burn they form oxides, **arsenic trioxide** (As_2O_3) and **antimony trioxide** (Sb_2O_3) respectively. The arsenic trioxide is the "white arsenic" of commerce. It is very poisonous and when mixed with a water solution of a copper salt it furnishes a valuable insecticide known as **Paris green.** The oxides are anhydrides of weak acids, which can be easily oxidized to arsenic acid (H_3AsO_4) and antimonic acid (H_3SbO_4). In these higher acids the elements have the valence of five.

Arsenic and antimony also show some of the characteristic properties of metals in that they form certain compounds which in water solution give a slight concentration of the ions, As^{+++} and Sb^{+++}.

BISMUTH

352. Bismuth. The last member of this family is a metal which shows only a few nonmetallic properties. It is not a very important substance. When heated strongly the metal burns, forming a trioxide (Bi_2O_3). This is essentially a basic oxide and forms salts, such as bismuth nitrate ($Bi(NO_3)_3$). If this nitrate is placed in water a white insoluble **basic** nitrate ($BiONO_3$) is formed, which is used in medicine as "bismuth subnitrate."

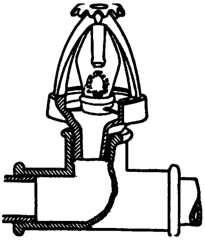


Fig. 202. Fusible plug of sprinkler system.

353. Useful alloys of antimony and bismuth. Bismuth is used in preparing alloys with very low melting points. For example, **Wood's metal,** which contains bismuth, lead, tin, and cadmium, melts at 60° C., a temperature lower than the melting point of any of the components. Such alloys are used in sprinkler systems. If a fire breaks out in a room provided with sprinklers plugged with this alloy, the plug (Fig. 202) soon melts and allows the water to gush out and extinguish the fire. These alloys are also valuable materials for safety plugs in steam boilers and for connecting links in devices which automatically close fire doors and curtains.

When antimony is added to lead and tin, the alloy obtained by melting them together is called **type metal**. This has the property of expanding slightly when it solidifies, which makes it useful in type founding. **Babbitt metal** contains the same metals in a different proportion, plus a little copper. It is used to line journal bearings in machinery. In such antifriction alloys the harder particles are pressed into the softer matrix (embedding material) so that a smooth surface is always presented.

THE PERIODIC SYSTEM

354. Properties of elements and their atomic weights. We have already pointed out that the elements may be grouped together into families, such as the halogen family or the nitrogen family. The Russian Mendelejeff (Fig. 203) was the first chemist who clearly showed how all the elements could be arranged according to a definite system. This is now called the **periodic system.**

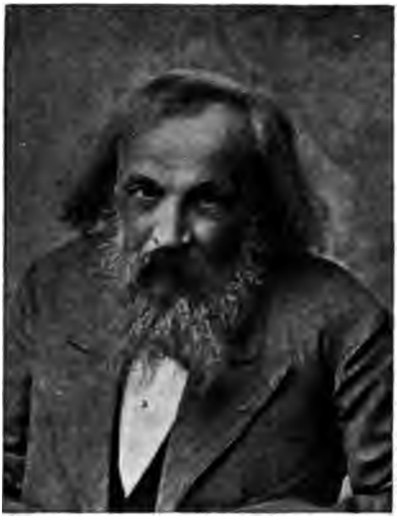


FIG. 203. MENDELEJEFF (1834–1907).

A Russian chemist to whom we are largely indebted for the periodic system.

If we arrange all the elements in the order of their atomic weights (omitting hydrogen), we shall find that the eighth and sixteenth elements are fluorine and chlorine respectively, two substances which resemble each other very closely. This relationship holds all through the first sixteen elements; if we write them as on page 345, we note that similar elements fall in vertical pairs, as, for example, *nitrogen* and *phosphorus.*

He(*4*)	Li(*7*)	Gl(*9*)	B(*11*)	C(*12*)	N(*14*)	O(*16*)	F(*19*)
Ne(*20*)	Na(*23*)	Mg(*24*)	Al(*27*)	Si(*28*)	P(*31*)	S(*32*)	Cl(*35.5*)

We express the fact that similar elements reoccur in the series at certain definite intervals by saying that *the properties of the elements are a periodic function of their atomic weights.*

355. The periodic classification. The table on page 346 shows nearly all the elements arranged according to such a periodic classification. It will be seen that the elements fall into nine general vertical groups, the first of which is called the zero group and the last the eighth group. The third horizontal row starts with argon and ends with three elements, iron, cobalt, and nickel, which are placed in the eighth group. The fourth row has no element in the zero group and is obviously somewhat different from the previous rows; it ends with the element bromine. The third and fourth rows of this table taken together are called the first **long period**; the first and second rows are called **short periods.** Again, the fifth and sixth lines together make a second **long period**; the seventh and eighth make a **long period.** It will be noticed that *a long period has in the middle of it three elements which are put together in the eighth group;* this seems to take the place of the empty space in the zero group.

We can show the relation of the elements still better by dividing each group into subgroups, or **families**, A and B. In the first two periods the first three elements are put in group A, the last three in group B. The elements which occur in the first half of each long period are placed in group A; those in the second half in group B. The zero and eighth groups have no subdivisions.

356. Valence. The first important fact to be noted about the periodic table is that *all the elements which occur in a group have the same valence toward a given element.* Below the group is written the typical formula for the oxide and for the hydrogen compound of members of that group. The elements in the

PERIODIC CLASSIFICATION OF THE ELEMENTS

PERIODS	0	I		II		III		IV		V		VI		VII		VIII		
		A	B	A	B	A	B	A	B	A	B	A	B	A	B			
First Short	**He** (4)	Li (7)		Gl (9)		B (11)		**C** (12)			**N** (14)		**O** (16)		**F** (19)			
Second Short	Ne (20)	**Na** (23)		**Mg** (24.3)		**Al** (27)		**Si** (28.3)			**P** (31)		**S** (32)		**Cl** (35.5)			
First Long	**A** (39.9)	**K** (39.1)	**Cu** (63.6)	**Ca** (40)	**Zn** (65.4)	Sc (44)	Ga (70)	Ti (48)	Ge (72.5)	V (51.2)	**As** (75)	**Cr** (52)	Se (79.2)	**Mn** (55)	**Br** (80)	**Fe** (56)	**Co** (59)	**Ni** (58.7)
Second Long	Kr (83)	Rb (85)	**Ag** (108)	**Sr** (87.6)	Cd (112)	Yt (89)	In (115)	Zr (90.6)	**Sn** (119)	Cb (93.5)	**Sb** (120)	Mo (96)	Te (127.5)	—	**I** (127)	Ru (102)	Rh (103)	Pd (107)
Third Long	Xe (130)	Cs (133)	**Au** (197)	**Ba** (137)	**Hg** (200)	La (139)	Tl (204)	Ce* (140)	**Pb** (207)	Ta (181)	**Bi** (208)	W (184)	—	—	—	Os (191)	Ir (193)	**Pt** (195)
	Nt (222)	—		**Ra** (226)		—		Th (232)		—		U (238)						
FORMULA OF OXIDE		R_2O		RO		R_2O_3		RO_2		R_2O_5		RO_3		R_2O_7		RO_4		
FORMULA OF HYDRIDE		RH		RH_2		RH_3		RH_4		RH_3		RH_2		RH				

* Between Cerium and Tantalum are several elements which are very similar. They have not yet been accurately studied, and so their position in the table is uncertain. The elements which are described in this book are printed in black-face type.

zero group will not combine and may be considered as having a zero valency.

It will further be seen from the oxides that as we proceed from left to right along any period the valence of the element increases regularly to the seventh. These regularities are very striking; when we remember that this classification of the elements is based solely on the position which they occupy in the series by virtue of their atomic weights, it is even more extraordinary. The elements which we are considering in this book are printed in heavy type in the table. The student may well familiarize himself with their position in the table.

357. The nonmetals. In the first two periods (which are short periods) the members of groups V, VI, and VII are active **nonmetals**; the elements of groups I and II are very active metals. In the long periods the three middle elements, which fall in group VIII, are all metals of a rather inactive sort; at the beginning of the period are active metals, and at the end of the period is an active nonmetal, such as bromine.

In order to see how valuable this periodic table is as a method of classification, let us consider the groups which contain the nonmetals. Group VIIB is the halogen family, which we have discussed in detail in an earlier chapter. We have already seen that there is a gradual change in properties as we proceed down the group from fluorine to iodine, the elements becoming less active. With group VIIA we need not concern ourselves. Group VIB contains oxygen, sulfur, and the two elements selenium and tellurium, which resemble sulfur very closely. We have previously called attention to the similarity between oxygen and sulfur.

Group VB is the nitrogen family, which we have just discussed. Nitrogen is a typical nonmetal having the valence of three in ammonia and a valence of five in the oxide (N_2O_5), which is the anhydride of nitric acid. Phosphorus forms a hydrogen compound with a formula PH_3 and an acidic oxide with a formula P_2O_5. Arsenic and antimony both form hydrogen compounds with the formulas AsH_3 and SbH_3, but these compounds are much less stable than ammonia. Arsenic and antimony also form acidic oxides in which the element has the valence of five. Bismuth does not form a hydrogen compound; its oxide, in which it has the valence of three, is a basic oxide and forms salts. Bismuth is in fact a typical metal. We notice in this group a gradual increase in the metallic properties of the elements as we proceed from nitrogen, a typical nonmetal, to bismuth, a typical metal. As a general rule, when we proceed down a group the elements become less active. In groups IV, V, VI, and VII this loss of activity is accompanied by a gain in metallic properties; the oxides become less acidic and more basic.

358. The metals. The very active metals sodium and potassium we find together in group IA. The less important elements lithium and rubidium resemble them closely. These metals form oxides which combine with water, giving very strong bases. We have already considered the close resemblance in this group between sodium and potassium. The elements which lie in IB and in group VIII are also metals, but of a different sort; they are not so active and their hydroxides are weak bases.

In general, we may sum up by saying that *in the periodic system the most active metals are at the top and to the left; the most active nonmetals to the top and to the right. Certain rather inactive metals lie in the middle of the long period and are found in groups VIII and IB. As we proceed down any group the elements become less active; the nonmetallic elements become more metallic.*

The essential characteristic of an element like sodium is its activity and the formation of a positive ion; this is sometimes called an extreme electropositive character. The essential characteristic of a nonmetal like fluorine is its activity and the formation of a negative ion; this is sometimes called an extreme electronegative character. With these definitions in mind we see that the most electropositive elements are in group IA, and the most electronegative elements in group VIIB. In between those extremes lie elements which represent the many gradations between these two opposite characteristics.

359. Value and use of the system. The periodic system is one of the greatest generalizations of all chemistry. While there are apparently numerous inconsistencies in special cases (as in the position of argon and potassium, also in the position of iodine and tellurium), yet on the whole it represents a very orderly arrangement and classification of a multitude of chemical and physical facts.

The table is of value *first* as a **means of classifying** what would otherwise be an almost hopeless and meaningless wilderness of chemical facts. In this way the system is useful not only to the student but also to the chemist and to the scientific investigator. For the latter it points the way to a more fundamental explanation of the whole science of chemistry.

The *second* great use of the system has been in the **prediction of the discovery of new elements.** When Mendelejeff first proposed his table, he was obliged to leave in it a number of blanks which he believed represented elements not yet discovered. On the basis of the position of these blanks he was able to predict with great accuracy not only the existence of these elements but their physical and chemical properties as well. His prediction was verified in three instances. The following table shows one of these; he prophesied the properties of what he called eka-aluminum, which when it was finally discovered was called **gallium.** There is hardly a scientific prediction in history that is more startling than this.

PROPERTIES OF GALLIUM	PREDICTED	FOUND
Atomic weight	about 69	69.0
Melting point	low	30.1°
Specific gravity	about 5.9	5.93
Action of air	none	slightly oxidized at red heat
Action on water	decomposes at red heat	decomposes at high temperatures

Finally, the system has been of use in the **revision of certain atomic weights.** A number of elements were thought at first sight not to fit into the table because of their atomic weights. In all but two or three instances a revision of the atomic weights showed that the earlier values were in error. There are still one or two elements whose atomic weights do not fit them into their proper place in the table. However, very recent developments have shown that the position of these elements is correct.

360. Position of hydrogen and the rare elements. The position of hydrogen in the system has been a matter of some discussion, but it is not of much consequence. It seems to be rather an odd element. Perhaps the best place for it is in group IA as it forms a positive ion. The rare gases fit very well into the zero group, and since they have no chemical activity, we do not have to concern ourselves with their valence.

SUMMARY OF CHAPTER XXVIII

THE NITROGEN FAMILY consists of nitrogen, phosphorus, arsenic, antimony, and bismuth.

PHOSPHORUS is an important constituent of plants and animals. The common allotropic forms are white and red.

White Phosphorus	**Red Phosphorus**
Melts at 44° C.	**Does not melt**
Very poisonous	**Not poisonous**
Low ignition point	**High ignition point**
Soluble in carbon disulfide	**Not soluble**
Phosphorescent in air	**Not phosphorescent**

Red phosphorus and the sulfide of phosphorus are *used* in the manufacture of matches.

ARSENIC AND ANTIMONY have a physical appearance resembling *metals.* They burn in air, forming oxides which are *acid anhydrides.* They both form certain compounds which give *a slight* concentration of trivalent positive ions. Arsenic com-

pounds are very poisonous. Antimony is a component of type metal and other alloys.

BISMUTH is a typical metal; it is used in making certain alloys which have a low melting point.

ALL THE ELEMENTS CAN BE ARRANGED in a table according to their *atomic weights.* The *properties of the elements are a periodic function of their atomic weights.*

THE PERIODIC SYSTEM classifies the elements into nine groups. All the elements in a group have essentially the same valence. The most active nonmetallic elements are at the top and right of the table; the most active metallic elements at the top and left. The elements in between have intermediate properties. As a rule the lower members of any group are less active than the higher members.

QUESTIONS AND PROBLEMS

1. What three other elements besides phosphorus have allotropic forms?

2. Why is red phosphorus considered more stable than white phosphorus?

3. What is the danger in using ordinary friction matches?

4. Sodium is kept under kerosene, white phosphorus under water. Explain.

5. What characteristics has arsenic which belong to a metal?

6. What essential characteristic has type metal which makes it useful?

7. Name three practical applications for Wood's metal.

8. What three elements are usually found in artificial fertilizers?

9. What does the phrase " periodic function " mean?

10. What natural processes might be called periodic?

11. Explain how group 0 (the inert gases) fits into the periodic system.

12. What properties would you expect lithium to have?

13. Give the formulas for strontium oxide, thorium oxide, and uranium oxide.

14. Calculate the percentage of phosphorus in calcium phosphate ($Ca_3(PO_4)_2$).

15. How much sulfuric acid will be required to treat 1 ton of phosphate rock? Assume the acid is 50% pure acid and the rock is 70% calcium phosphate.

16. Compute the atomic weight of phosphorus from the formula P_2O_5 and the fact that 18.585 grams of phosphorus give 42.584 grams of phosphoric pentoxide.

TOPIC FOR FURTHER STUDY

Fertilizers. Why does land need to be fertilized? What are the elements that must be supplied in the form of fertilizer? Is there an abundant supply of fertilizer material? What other factors affect crops besides fertilizers? (*Slosson's* Creative Chemistry, *Duncan's* Chemistry of Commerce, and pamphlets issued by the State and Federal Agricultural Stations.)

CHAPTER XXIX

SILICON AND ALUMINUM

Silica — properties and uses — silicic acid and silicates — glass — silicon — carborundum.

Natural aluminum compounds — manufacture of aluminum — properties and uses — thermite — alumina — aluminum hydroxide — alums — purification of water — clay — pottery and porcelain.

361. Silicon and aluminum compounds. Although neither of these elements occurs in nature in the free state, their compounds are found in great abundance. It will be remembered that silicon makes up about one-fourth of the whole crust of the earth and that aluminum is the most abundant of the metals.

It will help to fix in mind the properties of these elements and their compounds if we recall that silicon is in the same group (IV) as carbon. Like carbon it has a valence of four and has no metallic properties; its acid (H_2SiO_3), like carbonic acid, is weak. Unlike carbon it does not form a great multitude of compounds containing numerous atoms linked together in a chain. Aluminum is the only member of the third group which is at all well known or important. Its hydroxide has both acidic and basic properties. It thus lies between the extreme metals and the nonmetals.

SILICON

362. Silica (SiO_2). The commonest compound of silicon is the oxide (SiO_2) called silicon dioxide, or more usually **silica**; sand, sandstone, and certain other substances which are found in enormous quantities consist of silica. Its purest form is quartz, or rock crystal, which occurs in fine, clear, six-sided prisms. Sometimes it appears in colored forms due to impurities; thus, *amethyst* is violet, *rose quartz* pink, *smoky quartz* brown, and *milky quartz* white. Other varieties of silica are onyx, opal, and flint. Petrified wood is a kind of silica which has gradually replaced the wood fiber of a tree, changing it to stone.

Silica is also found in plants, especially in the leaves and stems, where it appears to give rigidity. Certain one-celled marine animals have skeletons containing silica. These animals belong to the **infusoria**; in some localities there are immense deposits of very fine sand called **infusorial earth** (Tripoli). This material is used to absorb nitroglycerin in making dynamite; also for removing coloring matters from oils and in making polishing powders.

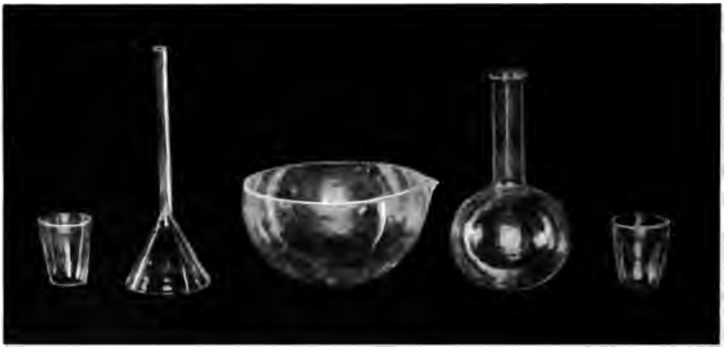


Fig. 204. Quartz laboratory apparatus.

363. Properties of silica. It is a hard, brittle substance and hence is used as an abrasive. **Sandpaper** consists of sharp quartz sand glued on paper. Silica can be melted in the oxyhydrogen flame and made into fine threads, tubes, flasks, *or crucibles (Fig. 204).*

Apparatus made of fused quartz does not expand or contract to any appreciable extent, even with considerable change in temperature. If we heat a quartz crucible red-hot in the flame of a blast lamp and then plunge it into cold water, it does not crack.

Quartz vessels are not attacked by the common acids. However, they are dissolved very rapidly by hydrofluoric acid (H_2F_2). Silica also dissolves in fused alkalies to form **silicates**:

$$2\,NaOH + SiO_2 \longrightarrow Na_2SiO_3 + H_2O$$

This reaction likewise takes place when silica is boiled with a concentrated alkali solution.

364. Silicic acid and silicates. Silicon dioxide is the anhydride of an acid with the formula H_2SiO_3 ($H_2O + SiO_2$); but this acid cannot be formed by dissolving silica in water. It is very weak and can be prepared only from its salts, the **silicates.** The silicates of calcium, magnesium, aluminum, and iron form the greater part of the earth's crust. Many of the common rocks, such as granite, are composed of minerals which are complicated and mixed silicates. Most of them are insoluble in water, but the alkali silicates are soluble.

Water glass, or sodium silicate (Na_2SiO_3), is made by fusing together silica and sodium carbonate:

$$Na_2CO_3 + SiO_2 \longrightarrow Na_2SiO_3 + CO_2 \uparrow$$

A solution of sodium silicate is an excellent preservative for eggs since it fills the pores of the shells and thus makes them air-tight. It is used to render wood or cloth fireproof, and as a cement for glass and pottery.

We add some hydrochloric acid to a solution of sodium silicate. The gelatinous precipitate is silicic acid:

$$Na_2SiO_3 + 2\,HCl \longrightarrow H_2SiO_3 \downarrow + 2\,NaCl$$

Silicic acid is precipitated when sodium silicate is acidified. The acid comes down as a gelatinous precipitate containing a rather indefinite amount of water. When heated sufficiently, the jelly loses all of its water and forms silica. Silicic acid is a very good example of a colloid.

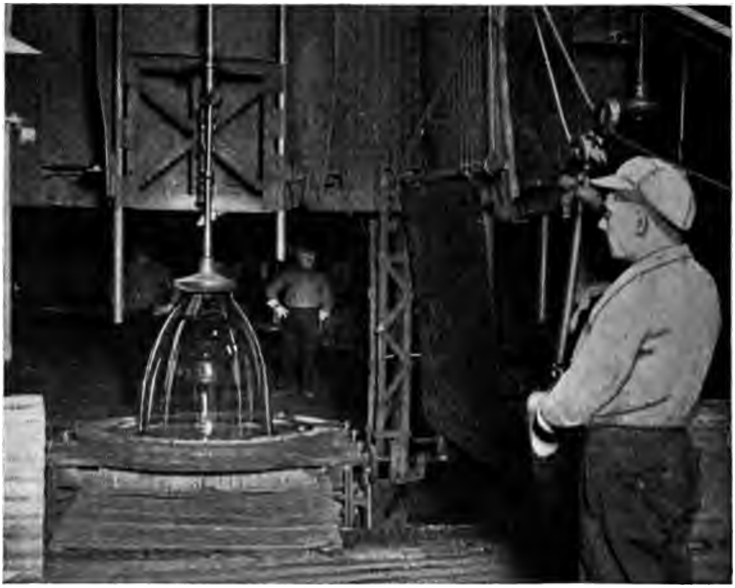


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Fig. 205. Mechanical blowing of cylinders for window glass.

365. Glass. Common glass is made by melting together sand, sodium carbonate, and calcium carbonate. At a high temperature the carbonates react with the sand, forming glass, a mixture of sodium and calcium silicates:

$$Na_2CO_3 + SiO_2 \longrightarrow Na_2SiO_3 + CO_2$$

$$CaCO_3 + SiO_2 \longrightarrow CaSiO_3 + CO_2$$

Such a mixture of silicates solidifies on cooling but does not *crystallize.* It stays as a transparent amorphous mass which may be considered as a supercooled solution of the one silicate in the other. On long standing certain grades of glass begin to crystallize, and this results in an opaqueness and a fragility of the glass. Hard glass, which melts at a higher temperature than ordinary, or soft glass, consists of a mixture of potassium and calcium silicates. Flint glass contains the silicates of lead, barium, and potassium.

In the manufacture of glass the ingredients are heated in a fire-clay pot by gas flames to a very high temperature. All the carbon dioxide must be expelled from the melt, otherwise bubbles and streaks will occur in the product. Traces of metallic oxides added at this point produce different colors in the glass. The cheaper grades are often somewhat green because of iron oxide.

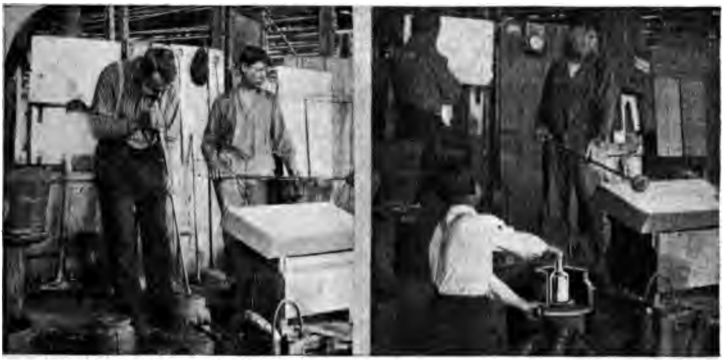

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Fig. 206. Glass bottles are blown in a mold.

Glass is worked into shape by blowing. A mass of the fused glass is taken on the end of a long blowpipe, and a skilled workman blows it into large cylinders or other desired shapes. Window glass is made from cylinders by cutting off the ends, slitting the cylinder lengthwise, and rolling it out as a plate while it is still soft. Mechanical blowers (Fig. 205) have now been introduced for making the larger cylinders. The apparatus automatically dips a large pipe into a kettle of molten glass, and then gradually raises it, pulling the molten glass upward as the pipe rises. A steady stream of air is kept flowing in through the pipe. Bottles and similar articles are formed by blowing the glass into molds either mechanically or by hand (Fig. 206).

Plate glass is manufactured by pouring molten glass on a table, rolling it with a hot iron, and finally carefully polishing it. *Flint glass* has peculiar optical properties and is used in the manufacture of lenses. Because of its brilliant appearance it is also made into ornaments, such as cut-glass vessels. The designs are cut by an emery wheel and then the object is polished with a very fine abrasive.

366. Silicon. This element is seldom seen because it is reduced from its compounds only with great difficulty. But silicon can be prepared by heating pure sand with carbon to a high temperature in an electric furnace:

$$SiO_2 + 2\,C \longrightarrow Si + 2\,CO \uparrow$$

It occurs as **amorphous silicon** in a brown powder and as **crystallized silicon** in black needles. Silicon is used as a deoxidizing agent in refining steel and in making iron alloys; also as a crystal detector in radiotelegraphy.

367. Carborundum. If the reaction between sand and carbon is carried out under certain conditions with a large excess of carbon, a compound of these two elements is formed, known as **carbon silicide,** or **carborundum.** An electric furnace (Fig. 207) similar to the one used in the manufacture of graphite is employed for this purpose. The core of the furnace is a mass of granulated coke. A mixture of sand, sawdust, coke, and a little salt is piled around the central core. The heat generated by the passage of a strong current through the coke is sufficient to cause the reaction to take place in the surrounding mass.

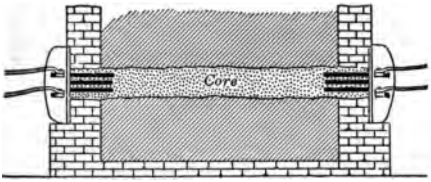

Fig. 207. Section of an electric furnace for making carborundum.

Carborundum is a crystalline solid with a beautiful purple color. It is extremely hard and is used as an abrasive in the form of *grinding* wheels and hones, and as a fine polishing powder.

ALUMINUM

368. Natural compounds of aluminum. Although aluminum is the most abundant metallic element, it is found in nature only in the form of compounds. **Bauxite**, a hydrated oxide of aluminum, is the source of the metal and of most of its compounds. In Greenland a double fluoride of aluminum and sodium is found which is called **cryolite** ($AlF_3 \cdot 3\,NaF$). Aluminum is also found as a constituent of all the common siliceous rocks, such as feldspar, clay, mica, and slate. **Emery**, a very useful and valuable natural abrasive, is an impure form of aluminum oxide (Al_2O_3), colored brown by iron oxide. **Sapphires** and **rubies**, which are highly prized as gems, are beautifully crystallized aluminum oxide.

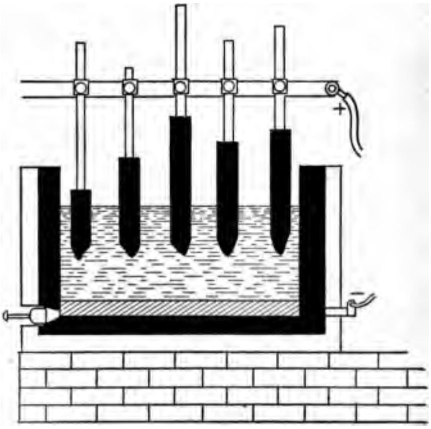

Fig. 208. **Diagram illustrating the making of metallic aluminum.**

369. Manufacture of aluminum. Because of the very great chemical activity of the element, aluminum oxide cannot be reduced to metallic aluminum by means of carbon in a furnace. The metal is now obtained by the **electrolysis** of its oxide. The process was discovered in 1886 by an American named Hall. The electrolyte for this process is a solution of aluminum oxide in *fused* cryolite; the cryolite is not changed during the process but serves only as a solvent. The oxide must be very pure and is prepared from bauxite by a long and careful process of purification.

The electrolysis is carried out in the apparatus shown in figure 208. An iron box is lined with amorphous carbon, which serves as the cathode. The anode is a set of carbon blocks suspended in the mixture. The cryolite is melted by the electric arcs which are formed when the current is first turned on. Aluminum oxide is added from time to time as the electrolysis proceeds. The metal is liberated at the cathode and collects as a liquid at the bottom of the box, from which it is drawn off into suitable molds. Oxygen is liberated at the anode and to a large extent burns up the carbon electrodes, which have to be renewed frequently. It requires only about 8 volts to keep the process going, but a current of several thousand amperes is needed.

370. Properties. Aluminum is a silver-white metal which usually has a rather dull surface due to a thin coating of the oxide. It is very light in weight, being only one-third as heavy as iron, and is an excellent conductor of both heat and electricity. It does not work well in a lathe and can be soldered only with difficulty.

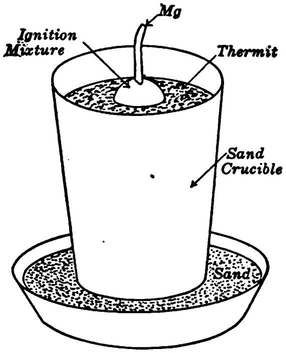

Fig. 209. Making molten iron by the use of thermite.

Aluminum is a moderately active metal, but because of the thin coating of adhering oxide which is always present it is not acted on by moist air, hot or cold water, or dilute sulfuric or nitric acids. Hydrochloric acid acts on it rather rapidly, producing hydrogen. It is dissolved by sodium or potassium hydroxide with the formation of compounds called **aluminates** and with the liberation of hydrogen:

$$6\,NaOH + 2\,Al \longrightarrow 2\,Na_3AlO_3 + 3\,H_2\uparrow$$

371. Uses. Aluminum is not so cheap as steel, and its use is therefore restricted to articles in which lightness is a prime essential, such as parts of automobiles and airplanes. It is sometimes used in the place of copper as a conductor of electricity. It is a very satisfactory material for cooking utensils, not only because of its lightness, but also because *it keeps bright, since the thin* film of oxide is transparent and protects the metal from further action of the air. Powdered aluminum is used extensively as a paint to protect other metals from corrosion. Very thin foil made of aluminum is replacing tin foil to some extent.

There are several important alloys of aluminum. Copper containing 5 to 12 per cent of aluminum is called **aluminum bronze**; it has a brilliant golden-yellow color. **Magnalium** contains a small amount of metallic magnesium. These alloys can be worked more easily than the pure metal.

372. Thermite. Metallic aluminum is a very powerful reducing agent. It reacts with the oxides of many metals, producing aluminum oxide and the free metal. This reaction takes place with the evolution of much heat and when once started proceeds vigorously. A mixture of aluminum and iron oxide is called **thermite.** When this mixture is ignited by means of a burning strip of magnesium ribbon, a reaction takes place, and a temperature of 3000° to 3500° C. is reached:

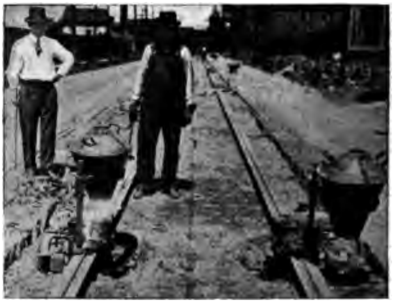

Fig. 210. Welding rails with thermite.

$$2\,Al + Fe_2O_3 \longrightarrow Al_2O_3 + 2\,Fe$$

Some thermite is placed in a sand crucible and on top of it a little heap of the ignition mixture consisting of sodium peroxide and powdered aluminum. Into this heap is inserted a piece of magnesium ribbon (Fig. 209). The crucible is then set into a pan of sand, and the magnesium ribbon is ignited. So much heat is developed that great care must be taken in doing the experiment. Very soon the crucible will contain liquid iron at the bottom and the fused slag on top. This is a good example of an exothermic reaction.

Advantage is taken of this reaction in **welding** rails (Fig. 210), shafting, and similar objects. The reaction is carried out in a cone-shaped crucible with a bottom opening. Extremely hot molten iron collects at the bottom and is allowed to run out on to the joint, which has been previously warmed to a red heat. The molten iron unites with the warm iron and makes a solid weld.

The same reaction enters into the preparation of **manganese** and **chromium** from their oxides. A mixture of powdered aluminum and the oxide is ignited; the free metal is thus produced.

373. Alumina. Aluminum oxide, or **alumina** (Al_2O_3), has already been mentioned. As it occurs naturally in a variety of forms and is extremely hard, it is extensively used as an abrasive. **Corundum** and **emery** are natural forms of aluminum oxide which are thus employed. **Alundum**, an artificial abrasive, is prepared by heating the oxide obtained from bauxite in an electric furnace until it just melts. Crucibles and muffles are often made of alundum because of its extremely high melting point.

The colors of ruby and sapphire, both of which are natural, crystallized aluminum oxide, are, as we have said, due to traces of impurity. Substances very similar to these are now prepared artificially by fusing aluminum oxide with a small amount of other metallic oxides to give the desired color. These artificial gems are chemically identical with the natural ones and can be distinguished from them only with great difficulty. Their preparation forms a very large and profitable industry.

374. Aluminum hydroxide. The hydroxide is formed as a colloidal precipitate when ammonium hydroxide is added to a solution of a salt of aluminum:

$$6\ NH_4OH + Al_2(SO_4)_3 \longrightarrow 2\ Al(OH)_3 \downarrow + 3(NH_4)_2SO_4$$

When heated, the aluminum hydroxide is decomposed into the oxide and water:

$$2\ Al(OH)_3 \longrightarrow Al_2O_3 + 3\ H_2O \uparrow$$

Aluminum hydroxide has both acid and basic properties. This means that it ionizes in two different ways:

$$Al(OH)_3 \longrightarrow Al^{+++} + 3\ OH^-$$

$$H_3AlO_3 \longrightarrow 3\ H^+ + AlO_3^{---}$$

It dissolves in most acids to form soluble salts, and in the strong bases to form aluminates:

$$Al(OH)_3 + 3\ HCl \longrightarrow AlCl_3 + 3\ H_2O$$

$$Al(OH)_3 + 3\ NaOH \longrightarrow Na_3AlO_3 + 3\ H_2O$$

375. Alums. When a solution of aluminum sulfate is mixed with a solution of potassium sulfate and evaporated, a double salt crystallizes out which has long been known as **alum** ($K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24\ H_2O$).

We prepare a saturated solution of alum and suspend in it a small alum crystal by a thread, as shown in figure 211. The small crystal grows and often becomes very nearly perfect.

This substance belongs to a class of compounds called **double salts**. We do not know the reason for their formation or for the way in which the atoms are joined together. There are a number of double salts which have the same crystalline form as ordinary, or potassium alum, and which have a similar formula; such as **ammonium alum** ($Al_2(SO_4)_3 \cdot (NH_4)_2SO_4 \cdot 24\ H_2O$) and **chrome alum** ($K_2SO_4 \cdot Cr_2(SO_4)_3 \cdot 24\ H_2O$). It should be noted that the last substance is called an *alum although it contains no aluminum.* Ordinary alum is the commonest form in which aluminum compounds are used.

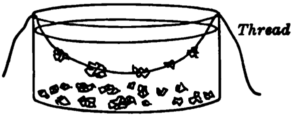

Fig. 211. Nursing crystals of alum.

376. Water purification. When aluminum hydroxide is precipitated in muddy water, it has the power of carrying down with it suspended particles. This property is used to advantage in the purification of water. Alum and lime are added in proper proportions to the contaminated water supply; the aluminum hydroxide which is formed carries down the suspended material from the water.

377. Clay and pottery. The purest form of clay, known as **kaolin**, is an aluminum silicate. This is a white substance formed by the decomposition of feldspar rock under the influence of weather over a long period of time. Feldspar is a potassium aluminum silicate which is slowly converted into soluble potassium compounds and kaolin. Impure, or ordinary clay is a mixture of kaolin with other substances, particularly iron compounds, which give it a red color.

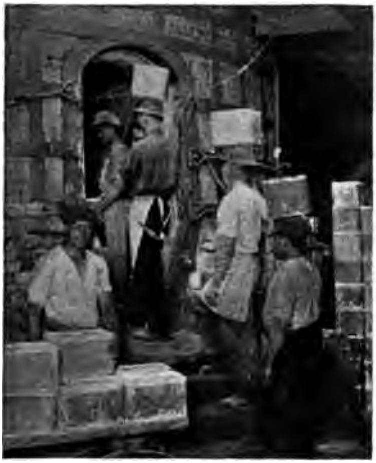

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Fig. 212. Filling a pottery oven with ware to be baked.

Bricks, tiling, flower pots, and similar porous stoneware are made of common clay. The clay is molded into the desired form and then baked in ovens fired generally with gas (Fig. 212). For many purposes the porous material must be covered with an impervious **glaze**. This is done by bringing salt into contact with the hot surface; a fusible sodium aluminum silicate is formed, which flows over it and on cooling solidifies to a hard mass. Cheap pottery is made in this way. Clay containing a large amount of silica is used for preparing fire bricks, stove linings, and other materials which are to be subjected to a very high temperature.

378. Porcelain. The pottery just described which is made by baking impure clay and putting on a superficial glaze is, as we have said, not of a very good quality. The better grades, **porcelain** and **china**, are made from pure white kaolin, feldspar, and quartz. The materials are ground fine, mixed with water, and molded into the desired shape. This may be done by hand with the help of a potter's wheel, or the mixture may be poured into a mold of plaster of Paris. When dry, the object is baked at a relatively low temperature until it is firm and hard but still porous. It is then covered with a thin coating of feldspar and silica and heated at a higher temperature and for a longer time. The thin coating melts and forms a glaze; according to the length of time of heating and the composition of the material, the latter also partially melts and fuses with the glaze. In such articles the glaze and the body of the material are thus melted practically into one mass. Colored decorations are put on by adding colored oxide to the coating which subsequently becomes the glaze.

SUMMARY OF CHAPTER XXIX

SILICON is a very abundant element which belongs to the carbon family. It can be prepared by heating sand and carbon in an electric furnace. With an excess of carbon a carbon silicide, *carborundum*, is formed.

SILICA is silicon dioxide, which is widely distributed as sand. Laboratory apparatus can be made from fused silica. Silica is dissolved by hydrofluoric acid and slowly by sodium hydroxide.

SILICATES are salts of silicic acid. This acid on heating decomposes into the oxide and water. The silicates are insoluble except those of sodium and potassium.

GLASS is a mixture of silicates. It is an amorphous solid. Ordinary glass is a mixture of sodium and calcium silicates. Hard glass contains potassium silicates. Flint glass contains the silicates of lead, barium, and potassium.

ALUMINUM occurs very extensively as oxides and silicates. The metal is made by electrolysis of the oxide dissolved in fused cryolite.

***The metal* is not attacked by moisture or air because of a thin coating of oxide. It dissolves in hydrochloric acid and in alkali solutions.**

THERMITE is a mixture of iron oxide and metallic aluminum. When ignited, metallic iron is produced at a very high temperature. Thermite is used in welding.

ALUMINUM OXIDE (alumina) is used as an abrasive and in the preparation of artificial gems.

ALUMINUM HYDROXIDE is both acidic and basic. It forms salts with acids and aluminates with bases. Certain double salts of aluminum are called *alums*.

CLAY is essentially an aluminum silicate. It can be baked into a hard porous form. A glaze can be put on by a suitable process.

QUESTIONS AND PROBLEMS

1. Name five important uses for silica.

2. What is the difference between water glass and ordinary glass?

3. What advantages has quartz glass for chemical apparatus? what disadvantages?

4. Compare carbon and silicon.

5. Why is an ordinary window not so smooth as plate glass?

6. How would you expect a solution of water glass to react with litmus? Explain.

7. Why is it sometimes difficult to remove the ground glass stoppers from bottles containing ammonium hydroxide?

8. What is the difference between silicon carbide and carbon silicide?

9. Name the ingredients of three different varieties of glass and give uses for each variety.

10. What has made aluminum a comparatively cheap metal?

11. If aluminum is the most abundant metallic element, why is it not the cheapest metal?

12. Why does the price of aluminum depend on the cost of electricity?

13. What are the especial advantages of aluminum for kitchen utensils?

14. What are the advantages of the thermite method of welding over other methods?

15. What would be the reaction of a solution of aluminum sulfate on litmus? Explain.

16. Make a list of the metals prepared by electrolysis.

17. Write the equation for the reaction of aluminum on hydrochloric acid.

18. How many liters of hydrogen (standard conditions) could be generated by the action of hydrochloric acid on 1 kilogram of aluminum?

19. Compare aluminum oxide and silicon dioxide.

20. Write the equation for the hydrolysis of aluminum chloride.

21. Calculate the percentage of water of crystallization in common alum.

22. Write the equation for the reaction of alum and lime ($Ca(OH)_2$).

23. Name two solid substances which are prepared commercially by heating sand with carbon.

24. Make a list of the abrasives mentioned in this chapter and give the formula of each.

25. Name two colloids which have been described in this chapter.

TOPICS FOR FURTHER STUDY

Glass and pottery. A number of industries and arts were developed long before the beginnings of the science of chemistry. Skilled craftsmen found by experience methods of producing such substances as glass and pottery. What chemical principles have recently been applied to these industries to bring about great improvements and economies? (*Duncan's* Chemistry of Commerce and *Findlay's* Chemistry in the Service of Mankind.)

Products of the electric furnace. What substances are now manufactured with the aid of the electric furnace? Would it have been possible to produce these materials before the electric generator was invented? How does this use of the electric current differ from that in the production of sodium hydroxide and chlorine or metallic aluminum? (*Duncan's* Chemistry of Commerce, *Slosson's* Creative Chemistry, *Cressy's* Discoveries and Inventions, and *J. C. Philip's* Romance of Modern Chemistry.)

CHAPTER XXX

MAGNESIUM AND CALCIUM

Magnesium, its preparation and properties — magnesium oxide and hydroxide — magnesium salts.

Calcium, its preparation and properties — calcium carbonate — hard water — methods of softening water — lime — calcium hydroxide — mortar — cement — other calcium compounds.

Strontium and barium.

379. General characteristics. We shall now study two elements, magnesium and calcium, which belong to Group II of the periodic system. Besides these there are two other less important members, strontium and barium. This family (IIA) is sometimes called the **alkaline earths**. The metal radium also belongs here, but it is such an unusual element that we shall devote a whole chapter (XXXVI) to its description. These elements are all very active metals which form positive divalent ions; they show no nonmetallic properties. We shall find that the properties of the metals and their compounds *vary in the order of the atomic weights.*

MAGNESIUM

380. Compounds found in nature. Magnesium occurs as **magnesite** ($MgCO_3$) and as a double carbonate **dolomite** ($MgCO_3 \cdot CaCO_3$). There are also several natural silicates of magnesium which are familiar and useful substances. These are **meerschaum**, **talc** or **soapstone**, and **asbestos**. Soapstone is used for sinks and table tops and when powdered is known as talcum powder or French chalk. Asbestos is a fibrous mineral, which is manufactured into fireproof cloth and cardboard. In the Stassfurt deposits magnesium occurs as a sulfate and as a double chloride with potassium.

381. Preparation and properties of the metal. Metallic magnesium is made by the electrolysis of fused salts, in the same way that such metals as sodium and aluminum are prepared. A mixture of magnesium, potassium, and sodium chlorides is used. A carbon rod forms the anode and an iron crucible the cathode. The molten metal collects on the sides and bottom of the crucible. When cold the mass is broken up and the metal removed. It is usually put on the market in the form of a fine powder or as a thin ribbon.

Magnesium is attacked by moist air and forms a white crust consisting of basic magnesium carbonate. It burns in air with a brilliant white light, producing the oxide (MgO) and the nitride (Mg_3N_2); **flashlight powder** consists of a mixture of magnesium powder and potassium chlorate. Certain kinds of **signal lights** and **fireworks** contain powdered magnesium. The metal reacts slowly with boiling water to form hydrogen:

$$Mg + 2\,H_2O \longrightarrow Mg(OH)_2 + H_2\uparrow$$

It displaces hydrogen rapidly from cold dilute acids.

382. Magnesium oxide and hydroxide. The oxide (MgO) is made by heating magnesium carbonate; it is called **magnesia.** It is a very infusible substance and is used for making fireproof bricks and the linings for high-temperature furnaces. It combines slowly with water, forming a hydroxide ($Mg(OH)_2$). This hydroxide is an insoluble white substance which finds some uses in medicine under the name of **milk of magnesia.** It is also formed when a soluble base like sodium hydroxide is added to a magnesium salt:

$$MgSO_4 + 2\,NaOH \longrightarrow Mg(OH)_2\downarrow + Na_2SO_4$$

383. Magnesium salts. Magnesium carbonate ($MgCO_3$) occurs naturally and is the source of magnesium oxide and hydroxide. It is insoluble in pure water but soluble in water containing carbon dioxide. A *magnesium bicarbonate* is formed:

$$MgCO_3 + H_2CO_3 \longrightarrow Mg(HCO_3)_2$$

Magnesium sulfate ($MgSO_4$) is a constituent of some natural waters and occurs in certain salt deposits. It is often called **Epsom salts** and is used in medicine because of its laxative properties. **Magnesium chloride** is found in sea water. In hot water this salt forms hydrochloric acid by hydrolysis:

$$MgCl_2 + H_2O \longrightarrow MgO + 2\ HCl$$

The acid corrodes metals, and hence sea water cannot be used in ships' boilers.

CALCIUM

384. Preparation and properties of the metal. Metallic calcium also is made by the electrolysis of a fused salt. Calcium chloride is used for this purpose.

The salt is fused in a graphite crucible, which forms the anode, and an iron rod is used as the cathode. The metal which is liberated around the rod adheres to it, and as this rod is gradually raised a stick of metallic calcium is pulled from the melt. It is a silver-white metal about as hard as lead and cannot easily be cut with a knife. It has a brilliant luster which is soon dulled by moist air. Water is slowly decomposed by calcium, and hydrogen is evolved:

$$Ca + 2\ H_2O \longrightarrow Ca(OH)_2 + H_2\uparrow$$

When heated to a temperature above its melting point it burns brilliantly, forming the oxide (CaO). Metallic calcium has few commercial uses.

385. Calcium carbonate ($CaCO_3$). This compound is the commonest form in which calcium is found. The purest variety is *Iceland spar,* which is crystalline and as transparent as glass.

Marble is almost pure calcium carbonate. It is composed of a mass of tiny crystals cemented together and is often as white as snow. **Limestone** is the most abundant form of calcium carbonate, but shows less of the crystalline structure than marble and is often of a cloudy gray color. We believe that limestone was formed in some previous geological age from the shells of sea animals.

Calcium carbonate is insoluble in water but like the magnesium compound is soluble in water containing carbonic acid, producing calcium bicarbonate:

$$CaCO_3 + H_2CO_3 \longrightarrow Ca(HCO_3)_2$$

Calcium carbonate reacts with acids, giving carbon dioxide:

$$CaCO_3 + 2\ HCl \longrightarrow CaCl_2 + H_2O + CO_2 \uparrow$$

Pure calcium carbonate can be made in the laboratory by adding some soluble carbonate to a soluble calcium salt:

$$Na_2CO_3 + CaCl_2 \longrightarrow CaCO_3 \downarrow + 2\ NaCl$$

Prepared in this way it is a white powder called **precipitated chalk** (not crayon) and is used in polishing powders (tooth paste); as **whiting** it is mixed with linseed oil to make **putty**. The natural forms of calcium carbonate are put to many uses besides that of preparing lime and carbon dioxide; for example, it is used as a flux in blast furnaces, in making soda and glass, as well as for a building stone and as ballast for roads.

386. Hard water. All natural water except rain water contains a certain amount of dissolved salts. Water in which there is a considerable amount of certain dissolved material is called **hard water.**

Magnesium and calcium bicarbonates are among the chief ingredients of the hard water which is found in some localities. These materials can very easily be dropped out of solution by simple boiling; carbon dioxide is expelled and the insoluble carbonate is precipitated:

$$Ca(HCO_3)_2 \longrightarrow CaCO_3\downarrow + H_2O + CO_2\uparrow$$

The hardness due to these salts is called **temporary hardness.** Salts such as magnesium sulfate and calcium sulfate cannot be removed by simple boiling, and water containing them is said to be **permanently hard.** In certain limestone regions all the water contains a great deal of temporary hardness. If it drips from some high place, as for instance from the top of a cave, it loses some of its carbon dioxide and slowly precipitates calcium carbonate. This material often accumulates in the form of long strips like icicles. The **stalactites** and **stalagmites** found in certain limestone caves are formed by this process (Fig. 213).

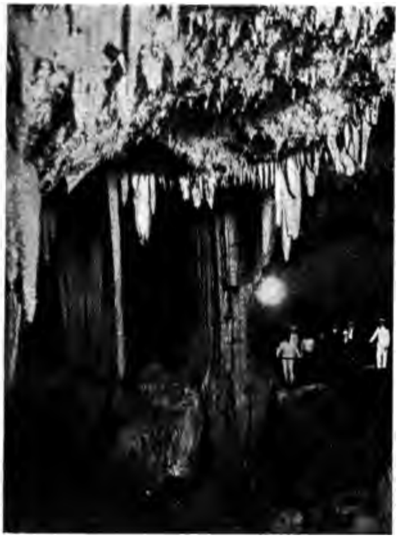
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Fig. 213. Limestone caves — stalactites and stalagmites.

Hard water is very undesirable for industrial and household use for two reasons. In the first place, when such water is used in a boiler, it deposits on the inside a heavy crust called **boiler scale.** This crust is a very poor conductor of heat and greatly cuts down the efficiency of the boiler (Fig. 214). In the second place, hard water is unsuitable for washing purposes because it will not easily form a lather with soap. Soap reacts with salts of calcium and magnesium, producing *insoluble calcium* and magnesium salts of the fatty acids:

$$2\,C_{17}H_{35}COONa + MgSO_4 \longrightarrow (C_{17}H_{35}COO)_2Mg + Na_2SO_4$$

These salts (often called **calcium** or **magnesium soaps**) are insoluble and form sticky particles in the water. Considerable soap must be used up in this way before the colloidal solution of soap is produced and a lather can be formed. This is, of course, very wasteful.

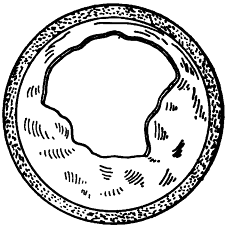


Fig. 214. Boiler scale in a tube.

387. Methods of softening water.

Hardness may be removed from water by a number of different methods; the process is called **softening water.** *Temporary hardness may be removed by* **boiling** *the water* for a short time; the insoluble carbonates are thus precipitated:

$$Ca(HCO_3)_2 \longrightarrow CaCO_3\downarrow + H_2O + CO_2\uparrow$$

Temporary hardness can also be removed by the action of ***lime;*** this is done by stirring the water with the exact amount of lime necessary to cause the following reaction to take place:

$$Ca(HCO_3)_2 + Ca(OH)_2 \longrightarrow 2\,CaCO_3\downarrow + 2\,H_2O$$

The precipitate is then filtered from the softened water.

Permanent hardness cannot be removed by these methods. Sodium carbonate will remove permanent hardness by precipitating calcium or magnesium carbonates:

$$CaSO_4 + Na_2CO_3 \longrightarrow CaCO_3\downarrow + Na_2SO_4$$

Industrially the softening of water is carried out on a large scale, and the precipitated material is filtered off from the water, which is then ready for use. In the household the softening is often brought about on a small scale by the use of certain preparations which are widely sold. Sodium carbonate under the name of **washing soda** is often employed. A small amount of it is added directly to the water before the soap is introduced. It removes all temporary and permanent hardness, as just explained. An excess of sodium salts has no deleterious effect on the soap. Ammonium hydroxide under the name of **household ammonia** is often employed in washing. It precipitates calcium carbonate from temporary hard water and from water containing both permanent and temporary hardness. Ammonium carbonate, formed from the calcium bicarbonates, acts like washing soda in removing permanent hardness:

$$Ca(HCO_3)_2 + 2\,NH_4OH \longrightarrow CaCO_3\downarrow + (NH_4)_2CO_3 + 2\,H_2O$$

$$CaSO_4 + (NH_4)_2CO_3 \longrightarrow CaCO_3\downarrow + (NH_4)_2SO_4$$

Magnesium salts cannot be precipitated in this way. Borax ($Na_2B_4O_7$) is a salt of a very weak acid, and therefore its solution contains sodium hydroxide, which acts like ammonium hydroxide in softening the water.

A new method of softening water, called the **permutite process**, consists in filtering the water through an artificial sodium silicoaluminate. The calcium and magnesium in the water are exchanged for sodium in the permutite, a coarse sand-like material (Fig. 215). After 12 hours' use one tank (Fig. 216) is filled with brine and allowed to stand the same length of time, while the sodium in the brine replaces the calcium in the filter. Then the calcium chloride solution is drained off and the filter is again ready for use. Thus we see that only salt is consumed, and the original charges last for years.

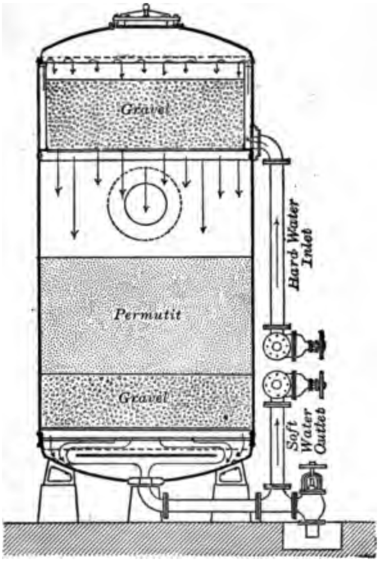


Fig. 215. Diagram of a permutite tank.

For convenience, the permutite radical may be indicated by Pe and the process of softening water as follows:

$$Na_2Pe + CaSO_4 \longrightarrow CaPe + Na_2SO_4$$

The reaction for the regeneration of the filter by brine is as follows:

$$CaPe + 2\,NaCl \longrightarrow Na_2Pe + CaCl_2$$

388. Lime, or calcium oxide (CaO). When limestone ($CaCO_3$) is heated it gives off carbon dioxide, and calcium oxide is left as a solid:

$$CaCO_3 \rightleftharpoons CaO + CO_2\uparrow$$

This reaction is reversible, and unless the gas is continually removed the action works backward. The process is carried out on a large scale in a furnace called a **kiln** (Fig. 217).

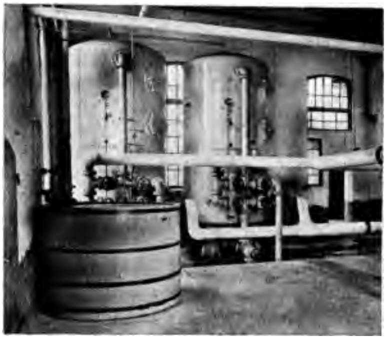


Fig. 216. Permutite water-softening plant.

The hot gases from a suitable fire pass through the coarsely ground limestone, which is thus heated to the desired temperature. The calcium carbonate decomposes according to the reaction previously given, and the carbon dioxide is removed by a strong draft through the kiln. In this way the action goes to completion at about 700° to 800° C. The product is often called **quicklime.**

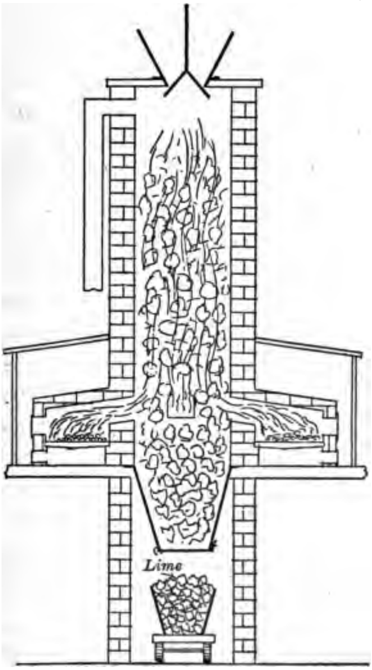


Fig. 217. Modern limekiln.

389. Properties and uses of quicklime. Quicklime is a white amorphous substance. It can be melted only with the greatest difficulty. When heated strongly, it glows with a brilliant light and hence was formerly employed in **limelights.** Calcium oxide combines with water very rapidly and vigorously to form calcium hydroxide:

$$CaO + H_2O \longrightarrow Ca(OH)_2$$

The reaction takes place with the evolution of much heat; it is called **slaking.** When exposed to air, quicklime slowly absorbs carbon dioxide and moisture. It is then said to be air-slaked and cannot be used for most purposes.

390. Calcium hydroxide, or slaked lime ($Ca(OH)_2$). The chief use of quicklime is in the preparation of **calcium hydroxide,** or, as it is often called, **slaked lime.** The hydroxide is a white substance, only slightly soluble in water. A clear solution is called **limewater.** A suspension of the hydroxide in water is called **milk of lime** and is generally employed when we wish to use calcium hydroxide.

Calcium hydroxide is a fairly strong base although we cannot obtain concentrated solutions of it because of its insolubility. In dilute solutions it is almost completely ionized. It is a very cheap substance and is therefore selected whenever an alkali is desired of which a concentrated solution is unnecessary. It is used to remove the hair from hides. Finely ground limestone and air-slaked lime are added to soils to neutralize their acidity. Lime is also employed very extensively as **whitewash** and in the preparation of **plaster** and **mortar.** It is usually prepared as needed by the slaking of quicklime; it is the latter substance which is generally sold under the name of lime.

391. Mortar and plaster. Mortar is a *mixture of slaked lime and sand.* It is used for holding together bricks and stone in the construction of buildings, walls, etc. It is exposed to the air for a long period in contact with a porous surface and under these conditions sets to a hard mass, which effectively binds the materials together. The setting of mortar is due largely to the absorption of carbon dioxide from the air and to the production of calcium carbonate:

$$Ca(OH)_2 + CO_2 \longrightarrow CaCO_3 + H_2O$$

We may put some pieces of old plaster in a test tube and add hydrochloric acid. The effervescence shows the presence of the carbonate. The sand is left behind undissolved by the acid.

Some of the moisture in the original mortar is lost by evaporation *and through* the porous bricks; this contributes also to the formation of a firm, hard mass. The crystals of calcium carbonate interlace with the sand and form a rigid though porous structure. This porous structure facilitates the entrance of more carbon dioxide into the interior of the mass and enables all the mortar to set.

Plaster is also made from freshly slaked lime and sand, but it generally contains hair in addition. This material serves to hold it together. The setting of plaster is exactly like that of mortar. Recently a mixture of lime and cement has come into use, which makes the use of hair unnecessary. An outer coating consisting of lime and plaster of Paris together with a little glue is put on when the plaster is nearly dry.

Plaster of Paris is made by heating gypsum ($CaSO_4 \cdot 2\,H_2O$) until about three-fourths of the water of crystallization is driven off:

$$\underset{\text{gypsum}}{2\,CaSO_4 \cdot 2\,H_2O} \longrightarrow \underset{\text{plaster of Paris}}{(CaSO_4)_2 \cdot H_2O} + 3\,H_2O$$

We mix enough plaster of Paris with water to make a stiff paste. We then put a medal on a glass square, oil them both, and pour the paste over the medal allowing it to dry for half an hour; the **plaster cast** is then removed.

Plaster of Paris takes up water of crystallization and forms a hard mass. It is therefore also useful for making copies of statuary and for surgical bandages.

392. Cement. Mortar depends for its setting on the loss of moisture and absorption of carbon dioxide. For this reason it cannot be used under water. A material called **cement** will set to a hard rock-like mass even under water; it can therefore be employed in the construction of dams, foundations for bridges, and similar objects. It is also superior to mortar and plaster in strength and firmness.

Cement is made by heating a mixture of limestone and clay, or of natural rocks which have these constituents in the proper proportion. The mixture is pulverized to a fine powder and slowly fed into an

inclined revolving cylinder, through which hot gases from a fire are passed (Fig. 218). In this way the material is subjected uniformly to the required temperature and finally falls out of the end of the revolving cylinder. The "clinker," as it is called, is cooled and ground to a very fine powder. In the process of heating, a certain amount of water and carbon dioxide is driven off from the mixture. When this dehydrated powder is made into a paste with water, it slowly unites with some of the water and forms a material as hard as rock. It resembles a stone found in Portland, England, whence the name Portland cement.

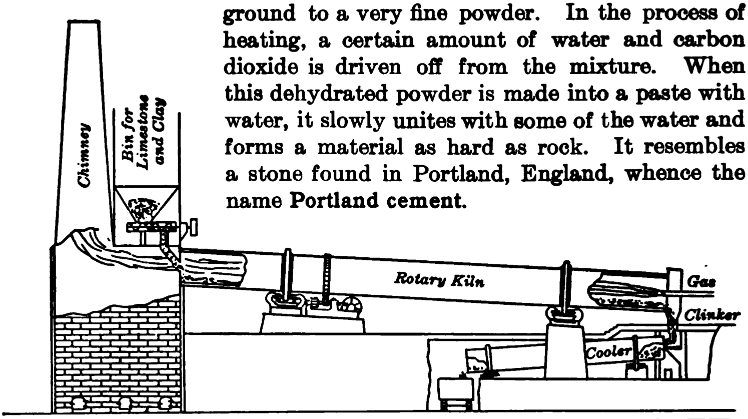


Fig. 218. Rotary cement furnace.

The chemistry of the setting of cement is not well understood. It involves the *hydration of the silicates* in the mixture and probably also of calcium oxide. The crystals of the hydrated silicates and of calcium hydroxide interlace and form a hard and compact mass.

Concrete is a mixture of cement, sand, and crushed stone or gravel made into a paste with water. It sets in the course of a few days to a solid mass, which is much harder and has greater strength than pure cement. Cement is never used alone but always as an ingredient of concrete. The latter has rapidly come to be one of the most important of building materials. It is used for making bridges, foundations, dams, walks, fences, and almost every sort of conceivable structure. When the concrete is to stand any severe tensile stress, as in the case of floors of buildings, steel rods or bands are embedded in it before it sets. This gives the mass much greater strength; such a material is called **reënforced concrete** (Fig. 219).

393. Other calcium compounds. Among the other important compounds of calcium are **bleaching powder** ($CaCl(OCl)$), **calcium carbide** (CaC_2), and **calcium cyanamide** ($CaCN_2$), all of which are prepared from lime. **Calcium chloride** ($CaCl_2$) is found in sea water and is also a by-product of the Solvay process. In granular anhydrous form it is very deliquescent and hence is used for drying gases. A saturated solution freezes at –48° C.; it forms the brine in refrigerating appliances. **Calcium fluoride** (CaF_2) occurs naturally and is the chief source of fluorine compounds.

Fig. 219. Reënforced-concrete building in process of construction.

All calcium compounds give to a Bunsen flame an orange color.

STRONTIUM AND BARIUM COMPOUNDS

394. Strontium and barium occur in nature as sulfates and carbonates. Their compounds are much rarer than those of calcium and they find only a few limited uses. *Barium compounds color flames a yellowish green* and for this reason are used in the manufacture of fireworks.

We pulverize separately and with great care equal volumes of *barium nitrate*, *potassium chlorate*, and *gum shellac*, mix the powders gently but thoroughly on a piece of paper, place the mixture in an iron pan, and set fire to it. *This makes green fire.*

Barium chloride is a crystalline solid which is soluble in water. It is used in the laboratory as a test for sulfuric acid, barium sulfate being formed as a white precipitate:

$$BaCl_2 + H_2SO_4 \longrightarrow BaSO_4 \downarrow + 2\ HCl$$

Barium sulfate occurs naturally as **barite**, a white mineral which is used in the manufacture of paint and in coating paper.

Strontium compounds burn with a bright red flame. The nitrate ($Sr(NO_3)_2$) is used as red fire in pyrotechnics.

SUMMARY OF CHAPTER XXX

METALLIC MAGNESIUM is prepared by the electrolysis of fused magnesium salts. It is an active metal and unites with nitrogen. It burns with a very intense white light and is used in flash-light powders, fireworks, and in the alloy magnalium.

MAGNESIUM OXIDE is prepared by heating the carbonate. It is very infusible and is used for making fire bricks. Magnesium hydroxide is a white insoluble substance.

METALLIC CALCIUM is prepared by the electrolysis of fused calcium chloride. It slowly decomposes water at room temperature.

CALCIUM CARBONATE occurs in many forms, such as marble, limestone, and chalk. It is insoluble in pure water but soluble in water containing carbon dioxide, the *bicarbonate* being formed.

HARD WATER contains dissolved salts. If the dissolved material is calcium or magnesium bicarbonates it can be thrown out of solution by boiling. This is called *temporary hardness*. Hardness which cannot be removed in this way is called *permanent hardness*.

Hard water forms a crust in boilers and *precipitates calcium* and *magnesium soaps* with soap solutions. Temporary hardness can be removed (1) by boiling or (2) by slaked lime. *Permanent hardness* can be removed by sodium carbonate. Sodium carbonate, ammonium hydroxide, and borax are used in the household for softening water. *Permutite* is used for softening water for industrial purposes.

LIME (calcium oxide) is made by heating calcium carbonate. Lime rapidly and energetically combines with water, forming calcium hydroxide (slaked lime). Calcium hydroxide is only slightly soluble in water.

MORTAR is a mixture of calcium hydroxide and sand. It hardens, or sets, by the evaporation of water and the absorption of carbon dioxide. Plaster is a mixture of calcium hydroxide, sand, and hair.

CEMENT is a partially dehydrated mixture of limestone and clay. When mixed with water it sets to a hard mass. This setting is due to the hydration of certain silicates and calcium oxide. *Concrete* is a mixture of cement, sand, and gravel.

Calcium compounds give an *orange* flame.

Strontium compounds give a *crimson* flame.

Barium compounds give a *greenish* flame.

Questions and Problems

1. What properties have the metals of this family in common?

2. Write the equation for the reaction of magnesium and dilute sulfuric acid.

3. How could you distinguish between Epsom salts and Glauber's salt?

4. In what two different ways could you obtain carbon dioxide from magnesite? Write the equations.

5. How could you show that the alkali metals are more active than the metals belonging to the family of alkaline earths?

6. What is the difficulty about using hard water in the household?

7. What are the consequences of using hard water in a steam boiler?

8. What are the results of using sea water in a ship's boiler?

9. What is the difference between air-slaked lime and limewater?

10. Why is it dangerous to let barrels of quicklime get wet?

11. Compare the hardening of mortar with the hardening of plaster of Paris.

12. Explain why air-slaked lime can be used to " sweeten " soil.

13. Could you use a barium hydroxide solution in place of limewater in testing for carbon dioxide?

14. Write the equation for making calcium hydroxide into calcium acid sulfite ($Ca(HSO_3)_2$).

15. How could you obtain barium sulfate from barium chloride?

16. How much quicklime could be made from one ton of limestone which is 97% pure calcium carbonate?

17. What weight of water would be needed to slake the lime made in Problem 16?

18. How many liters of carbon dioxide at 18° C. and 75 cm. pressure could be obtained from 1 kilogram of calcium carbonate?

REVIEW QUESTIONS

1. What is bleaching powder? How is it made?

2. Name not less than five elements which would color a Bunsen flame and give the color in each case.

3. Give the formula and state one use of each of the following: *sal-ammoniac, cream of tartar, graphite, plaster of Paris, cooking soda, quicklime, vinegar.*

4. State briefly how you would prove that the atmosphere contains (*a*) nitrogen, (*b*) carbon dioxide, (*c*) water vapor.

5. What elements occur commonly in organic substances? How can their presence be shown?

TOPIC FOR FURTHER STUDY

Soft and hard water. Is the water used in your household soft? How easily does it lather with soap? Compare it with rain water. Does any precipitate form on the inside of the teakettle? How effective is washing soda in removing any hardness which you may find? Try some of the cleansing or soap powders recommended for use with hard water. How is water purified for industrial use? (***Thorp and Lewis's*** Outlines of Industrial Chemistry.)

CHAPTER XXXI

IRON AND STEEL

Iron ores — smelting — blast furnace — cast iron — wrought iron — steel — microscopic study of iron — crucible steel — Bessemer steel — open-hearth process — electric furnace — hardening and tempering of steel — case hardening — special steels and iron alloys — comparison of irons and steels.

395. Importance of iron. Iron is doubtless the most valuable metal in the world. Not that it is so costly; indeed, its value rests upon its cheapness and its adaptability to an enormous number of uses. It has in fact become a necessity in our modern life, and we are said to live in **the age of steel and concrete.** Particularly in our own country has the industry of iron and steel production reached such huge proportions that *the yearly output approximates thirty million tons.* For the development of this industry chemical knowledge and engineering have been required. In our present chapter we shall discuss methods of iron and steel production.

396. Iron ores. The principal compounds of iron which occur naturally are various forms of the oxide, the carbonate, and the sulfide. Of these the oxides are the chief source of metallic iron. The most important **iron ores** are hæmatite (Fe_2O_3), magnetite (Fe_3O_4), limonite ($Fe_2O_3 \cdot 3\,H_2O$), and siderite ($FeCO_3$).

Metallic iron is obtained from these oxides by the action of carbon and carbon monoxide at a high temperature. The production of a metal from its ores is often called **smelting.** Iron ore is never pure iron oxide but always contains certain amounts of other mineral matter, such as quartz or limestone. For this reason the smelting must be done in such a way that these impurities can be conveniently removed.

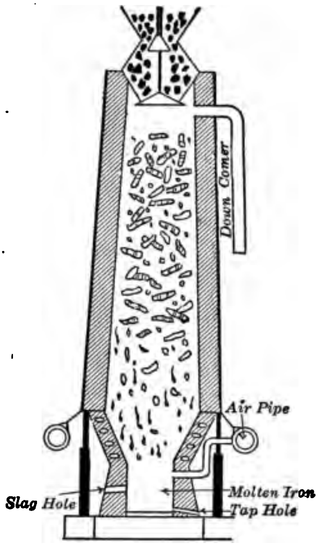


Fig. 220. Diagram of a blast furnace.

397. The blast furnace. The production of iron from its ores is carried on in an apparatus called a **blast furnace**. It consists of an iron structure 60 to 90 feet high lined with fire brick (Fig. 220). Near the bottom of the furnace are a number of pipes called **tuyeres**, which allow a stream of hot air to be blown into the furnace. This air is usually dried by first cooling it to a low temperature, the water condensing out in the form of ice. Before the dry air enters the furnace it is preheated by means of the so-called **stoves** shown as towers in the picture (Fig. 221). *The charge consists of a mixture of the **ore, coke,** and a substance called a **flux**.* The purpose of the flux is to combine with the rocky impurities in the ore. When the impurity is mostly silica, the flux is limestone; if the impurity is limestone, the flux is silica. The resulting compound in either case is calcium silicate and is called **slag**. The slag melts at a lower temperature than either the impurities or the flux, and this causes the whole mass to begin to soften at a relatively lower temperature; hence the name flux (a flowing). The heat required for the process is generated by the combustion of the coke in the lower half of the furnace. Carbon dioxide is first formed but is immediately reduced to carbon monoxide by the red-hot coke. Carbon monoxide ascends and meets the iron oxide in the upper half of the furnace and there reduces it to iron:

$$Fe_2O_3 + 3\,CO \rightleftharpoons 2\,Fe + 3\,CO_2$$

This reaction is reversible, and it is necessary to have an excess of carbon monoxide in order to carry it through. Therefore the gases which escape contain 20 to 35 per cent of carbon monoxide. They are combustible and are burned in the stoves which preheat the incoming air.

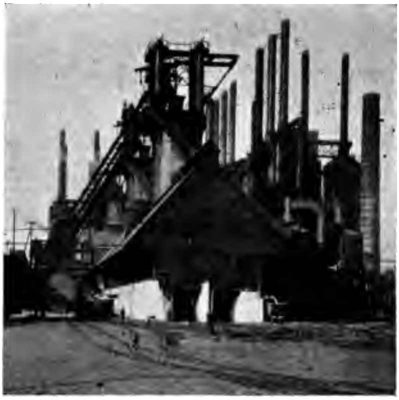


Fig. 221. Blast furnace and its stoves.

The charge is fed in through the hopper at the top and slowly descends through the furnace. The iron and slag begin to melt and flow when they reach the lower part of the furnace. The complete reduction of iron oxide then takes place by means of hot carbon:

$$Fe_2O_3 + 3\,C \rightarrow 2\,Fe + 3\,CO$$

The slag and the molten iron form two layers; the latter, being heavier, is at the bottom. The furnace is tapped from time to time at the proper points, and the iron and slag are separately run off. A blast furnace is kept in continual operation; it is not necessary to interrupt it until the lining has been worn out. Figure 222 shows by a diagram what *goes into* the furnace and what *comes out.*

398. Cast iron. The molten iron from the blast furnace is run into sand molds or a continuous belt of iron molds (Fig. 223); the resulting metal is called **cast iron** or **pig iron.** It is impure metallic iron and contains about 5 or 6 per cent of impurities including silicon, manganese, sulfur, phosphorus, and carbon. The latter is present in relatively large amounts, varying from 3 to 5.5 per cent. The other impurities exist in less amounts. Pure iron melts at 1510° C., but because of the presence of the impurities cast iron melts at about 1100° C.

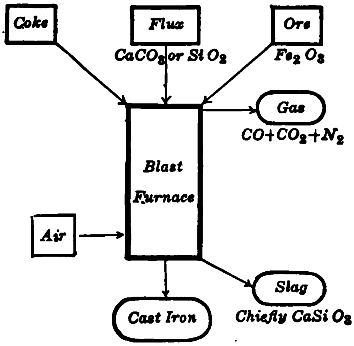


Fig. 222. Diagram showing what goes into and what comes out of a blast furnace.

Pig iron can therefore be easily remelted and cast into any desired form. It expands on solidifying, and consequently the metal fills all the details of the mold and makes a very satisfactory casting. It is, however, brittle and has a rather low tensile strength. It cannot be welded. It is used for making such things as stoves, radiators, ornamental iron work, base plates, and other heavy parts of machines.

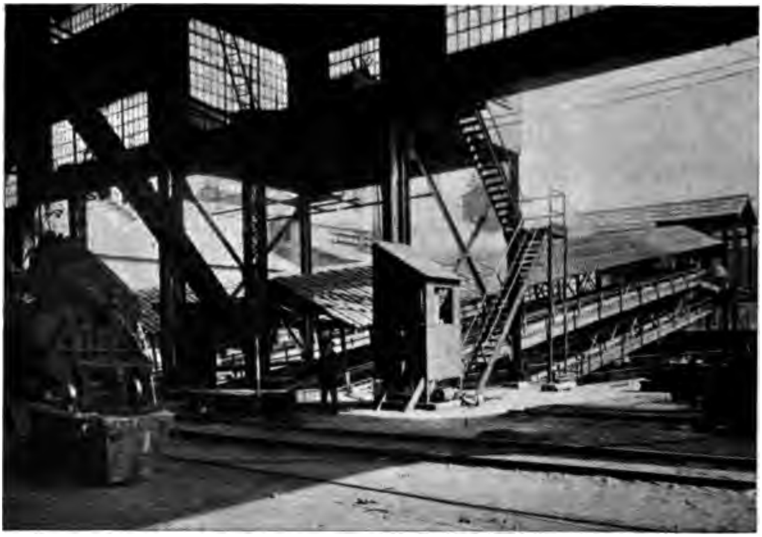


Fig. 223. Pouring molten iron into molds on an endless belt.

399. Wrought iron. Most of the impurities in cast iron can be removed by heating pig iron in contact with iron ore. This is done in a **reverberatory furnace** (Fig. 224). The hot products of combustion, which are deflected by the low roof, play upon the pig iron and melt it. Workmen with long rods stir the molten iron on a bed of iron ore and in this way bring it thoroughly into contact with the oxide, which in turn oxidizes the carbon and sulfur to volatile oxides. The phosphorus and silicon are oxidized to their oxides, and these combine with lime or some other basic oxide which is present and form a slag. As the impurities are extracted from the iron its melting point rises and it becomes thicker and thicker. Finally it is removed in balls on the ends of the iron rods. While still hot these balls are pressed out into bars, and the product is known as **wrought iron.**

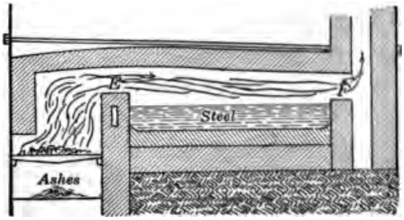
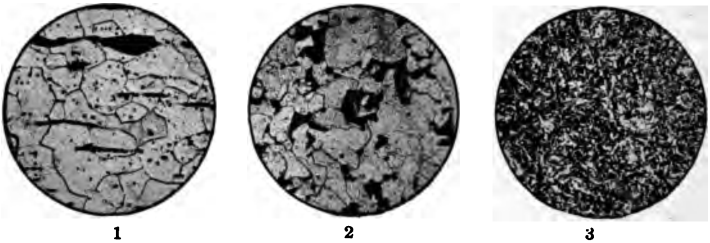


Fig. 224. **Diagram of reverberatory furnace.**

Wrought iron is a fairly pure iron (table on page 396) except for the small amounts of slag which always remain in it and give to it its fibrous structure. It is extremely tough and hence is used in the manufacture of articles, such as anchors and chains, which must stand severe and sudden stresses. It is not brittle and can readily be welded.

400. Steel. The amount of carbon in iron greatly influences its properties. It is probably present in the form of a compound called **iron carbide,** or **cementite** (Fe_3C). Wrought iron contains less than 0.2 per cent of carbon; cast iron, as we have seen, from 3 to 5.5 per cent. Between these extremes lie materials which are called steel and which contain usually between 0.60 and 1.5 per cent of carbon. As a matter of fact, considerable steel (called **mild steel**) is now manufactured which, as far as its carbon content is concerned (less than 0.2 per cent), is not different from wrought iron. Steel is more uniform and freer from slag than wrought iron. It also has a greater tensile strength. Wrought iron is always hammered out into the desired shape, whereas steel is first poured into a mold and the ingot is subsequently given a mechanical treatment, generally while still hot. In contrast with cast iron, steel is malleable and can be forged and rolled; as a rule it is not brittle and can be welded. Steel containing more than about 0.5 per cent of carbon can be hardened and tempered in such a way that it becomes very hard and brittle; wrought iron, cast iron, and mild steel cannot be hardened.

401. Microscopic study of iron and steel. In recent years the microscope has been used to study the structure of metals. When a specimen of iron or steel is polished and then suitably etched with weak acids, it is possible *to detect certain characteristic crystalline formations* under the microscope. Figure 225 shows such microphotographs of wrought iron, soft steel, and hardened tool steel. This study is known as **metallography,** and has already been the means of discovering a close relation between the microstructure and the physical properties of metals.



Courtesy of *Sauveur & Boylston.*

Fig. 225. Microphotographs of wrought iron (1), soft steel (2), and hardened tool steel (3).

402. Crucible steel. Small quantities of steel of a high quality are made by melting together in clay crucibles a mixture of iron and small amounts of iron oxide or charcoal. The iron which is taken for this purpose is usually scrap steel, wrought iron, and occasionally some very pure pig iron. If there is more carbon in the iron than is desired in the steel, a small amount of iron oxide may be added to oxidize part of it to carbon monoxide, which escapes. If, on the other hand, the iron is too low in carbon, charcoal is put into the mixture at the start. In making crucible steel it is possible to add any given substance to the melt in order that the desired product will be obtained. This process is essentially a simple mixing and melting together of the required ingredients; *relatively pure iron, however, must be used in the process.*

403. Bessemer steel. To convert ordinary cast iron into steel we must remove a large amount of the impurities. This can be done by the Bessemer process.

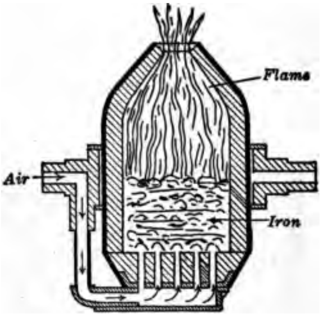


Fig. 226. Section of a Bessemer converter.

In this process an apparatus called a **converter** (Fig. 226) is employed; this is made of steel and is usually lined with silica brick. It has a false bottom so that a stream of air can be introduced. The melted pig iron is run into such a converter, which holds about 15 tons, and air is blown through the molten mass. The carbon, silicon, and manganese are oxidized, and the heat of this oxidation is sufficient to keep the mass fluid, although the impurities are removed as the melting point rises. The impurities are oxidized first, and the process is stopped before the iron itself begins to oxidize. As soon as the character of the flame (Fig. 227) shows that all the carbon has been burned away, just the desired amount of carbon (usually in the form of a high-carbon iron alloy) is added and allowed to mix with the liquid iron. The whole process is usually over in about 20 minutes, the converter is then tilted, and the material run out into ladles. A certain amount of slag floats on top of the steel, and the ladle is poured in such a

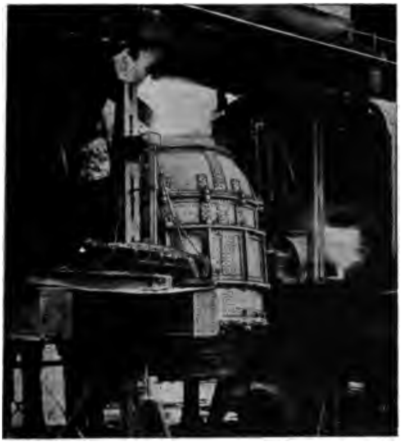


Fig. 227. Bessemer converter in action.

such a w ... he liquid steel is poured into iron
iron, cast ... steel wire, rods, and rails, the
401. ... agonal blocks. These ingots while
the mic ... rolled out into bars and other de-
When
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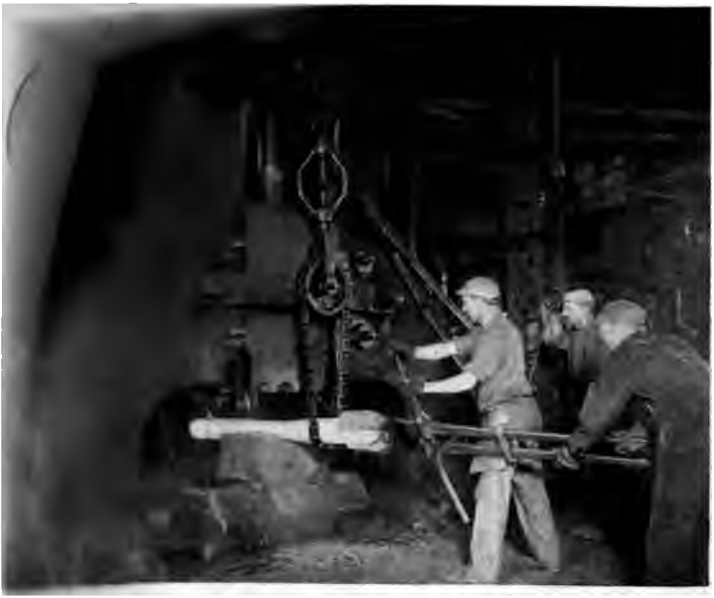

Fig. 228. Forging an axle with a hydraulic press.

quantities, are very deleterious to steel. Phosphorus causes it to be brittle at ordinary temperatures ("cold short"); sulphur has the same effect while it is being worked at a red heat ("red short"). If pig iron containing very much phosphorus is used in the Bessemer process the converter must be lined with dolomite ($CaCO_3 \cdot MgCO_3$). This is a basic lining, whence *the process* is termed the **basic Bessemer**; with the silica lining it is called the **acid Bessemer**. Under basic conditions phosphorus is removed as it is oxidized to the oxide, which then combines with the basic lining, forming calcium phosphate.

404. Open-hearth process. The basic Bessemer process described in the last paragraph is for a number of reasons not entirely satisfactory. The lining is expensive, is rapidly corroded, and can be used only with certain kinds of "phosphorus pig." The **open-hearth process** for making steel has now been widely adopted for pig iron which contains too much phosphorus for the acid Bessemer.

Here the pig iron and iron oxide, together with some flux, are heated by a flame of producer gas in the furnace shown in figure 229. In order to get the high temperature necessary to melt steel, a regenerative device has been employed. By its means the fuel gas and the air are preheated as they pass through some brick work, which itself has been previously heated by the effluent gases from the furnace. Oil burners are now used in connection with open-hearth furnaces, and powdered coal has been tried as a fuel. It is possible that by the introduction of a suitable liquid or solid fuel furnaces in the future will be run without the cumbersome regenerative gas system.

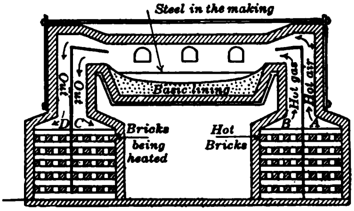

Fig. 229. Diagram of an open-hearth furnace.

The lining of the furnace may be either silica or dolomite, the processes being called the **acid open-hearth** and the **basic open-hearth** respectively. We shall confine our attention to the basic open-hearth process, which is used for pig iron containing phosphorus.

The charge consists of pig iron (often mixed with scrap steel), iron oxide, and lime. The carbon content of the pig iron is reduced by the action of the iron oxide:

$$Fe_2O_3 + 3\,C \longrightarrow 2\,Fe + 3\,CO$$

The iron oxide is added from time to time, and the molten mass "boils" with the evolution of carbon monoxide. The phosphorus and silicon are oxidized and pass into the slag by combining with the lime. This

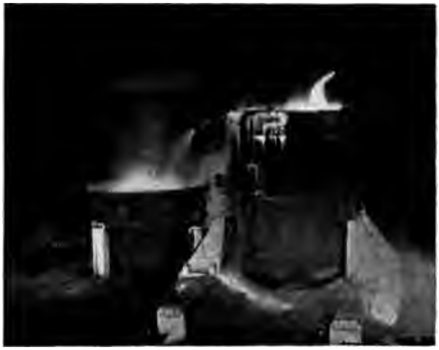

Fig. 230. Tapping an open-hearth furnace.

slag floats on top of the molten steel and protects it from the action of the hot flame, which would otherwise tend to oxidize the iron. The molten steel is tapped off in large ladles (Fig. 230). From these ladles the molten steel is poured into ingot molds (Fig. 231). The sulfur content can be lowered somewhat in the basic open-hearth process, but this method is essentially employed for removing carbon and phosphorus. Pig iron which is very high in sulfur requires a special treatment.

The basic open-hearth process has not only the advantage that it refines a phosphorus pig iron, but its product is also superior to that from a Bessemer converter. The reaction is slower and can be kept under better control. The product is more uniform, and because the melt is carried out under relatively quiet conditions, it contains less slag and dissolved gases.

Molten steel dissolves considerable quantities of carbon monoxide and other gases, which it liberates on cooling. These gases cause a porous structure in the steel ingot. The addition of small amounts of strong reducing agents to the melt *just before it is* poured helps

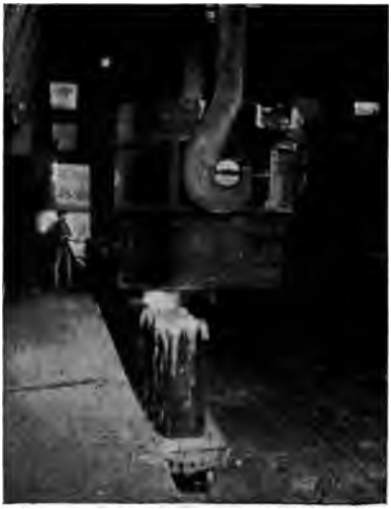

Fig. 231. Pouring steel ingots.

to remove the dissolved gases and to give sounder ingots. Metallic silicon (or ferro-silicon, an alloy of iron) and ferro-titanium are often employed, as is also metallic aluminum. Ferro-manganese (an alloy of manganese and iron) is also added at this point as a degasifier and as a means of introducing the small amount of manganese which is necessary for good steel.

405. Electric furnaces. The production of steel in electric furnaces (Frontispiece) has been developed to some extent and seems to have certain advantages. In one type of furnace, called the **Heroult** (Fig. 232), the heat is generated by the arcs between the carbon electrode and the molten metal. The reactions which take place in electric furnaces are much like those in the open hearth. They are always lined with a basic material and therefore readily remove phosphorus. Sulfur can pass into the slag only under reducing conditions. No strong oxidizing flame is present in an electric furnace as in an open-hearth furnace, therefore sulfur can also be eliminated. The electric furnace enables one to obtain a high temperature in a basic furnace without oxidation. For these reasons it is used for purifying steels made from low-grade pig iron and scrap.

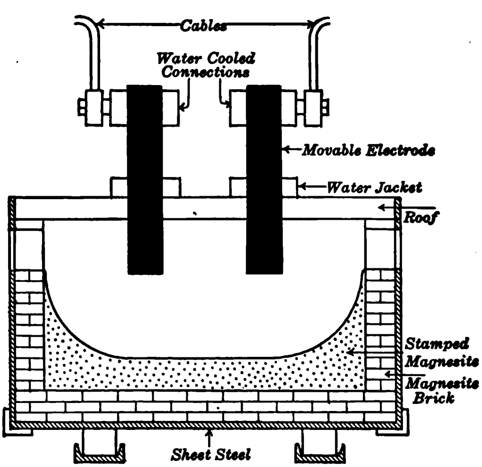

Fig. 232. Diagram of an electric furnace.

406. Tempering of steel. As has been said, the carbon in steel is present as iron carbide. When steel first solidifies, this iron carbide is in solution in an allotropic form of iron called

gamma iron, which is stable only at high temperatures. On cooling, a piece of steel passes through a number of rather complicated transformations at a temperature of 770° to 700° C. This range of temperature is called the **critical range**;[1] the transformations that take place involve the change of several allotropic forms of iron and the separation of iron carbide.

If the steel is slowly cooled through this range, the iron finally ends up as the **alpha modification**, and the iron carbide separates out in a certain crystalline condition. The resulting steel is comparatively soft. If steel containing more than 0.50 per cent of carbon is quickly cooled (quenched in water or oil) from above its critical temperature, the transformations taking place through the critical range are checked, and the resulting iron and iron carbide are left in such a form that a very hard, brittle steel is produced. Such steel is said to be **hardened**; the degree of hardness which results from the cooling depends somewhat on the carbon content of the steel. This steel is usually too brittle for most purposes and can be softened to varying degrees by heating to certain temperatures and then again quickly cooling. This process is called **tempering**. The higher the temperature to which we heat the steel in the tempering process, the more *the arrested transformations of the critical range can complete themselves* and the softer the steel will be. The temperature can be estimated by the play of colors which appear when the metal is heated. This is due to the formation of thin layers of iron oxides. Steel is usually first hardened by quenching it from a temperature above the critical range; it is then reheated to the desired temperature and quenched again. The following table shows the colors and temperatures for tempering various articles of commerce.

TEMPERATURES	COLOR OF OXIDE FILM	VARIOUS TOOLS
225° – 235° C.	Straw	Light turning tools
236° – 250° C.	Yellow-brown	Screw-cutting dies and taps
251° – 275° C.	Purple	Twist drills
276° – 300° C.	Blue	Saws and wood-working tools.

The yellow tints give very hard but brittle steels, while the blue give softer and tougher steels.

407. Case hardening. If wrought iron or mild steel is heated in contact with powdered charcoal it slowly takes up carbon. The carbon seems to penetrate the entire mass by degrees. This was the old **cementation process** of manufacturing what was known as **blister steel.** The same method, called **case hardening,** is now employed for producing a layer of high-carbon steel on a body of the softer metal. Such a steel on being properly hardened and tempered has a hard exterior and a tough interior. This process is used to give the desired hard surface to various parts of machinery, such as automobile gears; a similar method enters into the manufacture of armor plate.

408. Special steels and iron alloys. A number of so-called special steels have become of importance for certain distinct purposes. These materials are manufactured by the open-hearth or crucible process. Steel containing from 7 to 20 per cent of manganese is exceedingly tough and resistant to wear. It cannot be machined. It is used for making rock-crushing machinery, safes, and brake shoes. **Chromium** and **nickel** steels, in which a few per cent of one or both elements are present, have great tensile strength and are very suitable for making parts for automobiles. They have considerable elasticity and therefore conform to the stress in such objects as springs, frames, and axles. A steel containing 36 per cent of nickel is called **invar**; it is properly not a steel at all but an iron alloy. It has practically no *coefficient of expansion* and is therefore very valuable in the manufacture of scientific apparatus; pendulums are often constructed of it. An alloy of iron and nickel containing 46 per cent of the latter is called **platinite**; it has the same coefficient of expansion as platinum and is used instead of this metal for "sealing in wires" in electric-light bulbs.

Steels containing a considerable quantity of tungsten or molybdenum as well as chromium are called **high-speed steels.** They can be hardened and do not lose their hardness even when heated to a low red heat. For this reason they can be used on a lathe or similar machine at a high speed. The tools will cut while they are dull red. An element called **vanadium** when added in small amounts to certain special steels seems to be of great benefit. **Chromium-vanadium steels and chromium-nickel-vanadium steels are used in the automobile industry.**

COMPARISON OF IRONS AND STEELS

	PER CENT OF CARBON	STRUCTURE	HARDNESS	USES
Wrought iron	0.05–0.2	Fibrous	Soft	Wire, water and steam pipes, horseshoes, rivets.
Steel (low-carbon)	0.05–0.8	Granular	Moderately soft	Structural steel, shafts, axles, nails.
Steel (high-carbon)	0.8–1.6	Granular	Hard, if tempered	Tools, springs, permanent magnets.
Cast iron	3–5.5	Crystalline	Brittle	Castings, bases, and columns.

SUMMARY OF CHAPTER XXXI

THE PRINCIPAL IRON ORES are oxides. These are reduced to metallic iron by carbon and carbon monoxide in a blast furnace. A flux is added which combines with the rocky impurities to form a slag.

THE PRODUCT FROM THE BLAST FURNACE is *cast iron*. It contains 5 to 6 per cent of impurities, mostly carbon.

WROUGHT IRON is fairly pure iron except for mechanically held slag. It is made by heating cast iron in a reverberatory furnace on a bed of iron oxide. It can be welded and is malleable.

STEEL usually contains more carbon than wrought iron and less than cast iron. It can be cast and is malleable. It can also be welded. Low-carbon steel is very much like wrought iron; high-carbon steel can be hardened.

STEEL IS MADE in the *crucible process* from scrap steel and wrought iron, or very pure pig iron. *Steel* can be made from cast iron by (1) the Bessemer process, (2) the open-hearth process, (3) *the electric* furnace.

In the *Bessemer* process the molten metal is oxidized with air, the silica, carbon, and manganese being oxidized before the iron. The Bessemer converter is usually lined with silica and called the acid Bessemer; it may be lined with dolomite and is then called the basic Bessemer. The acid Bessemer process will not remove phosphorus or sulfur. The basic Bessemer will remove phosphorus, but is not very satisfactory.

The basic open-hearth is the usual process for handling phosphorus pig. The oxidation is carried out by an oxide, the heat being supplied by gas flames. Phosphorus is satisfactorily removed, sulfur is lowered somewhat.

The electric furnace, used for refining steel, gives a high temperature without an oxidizing flame. Phosphorus, sulfur, and other impurities are removed in it.

THE HARDENING OF STEEL containing more than about 0.50 per cent of carbon can be done by heating above 700°–770° C., called the *critical range*. If the changes through this range are arrested by sudden cooling, a very hard steel results. This can be softened, or *tempered*, by reheating; the higher the temperature of reheating the softer the steel becomes. A layer of high-carbon steel can be put on a mild steel by *case hardening*.

SPECIAL STEELS: *Manganese steel* is very tough. *Chromium and nickel steels* are strong and somewhat elastic. They are used in making automobile parts. *Invar*, an iron-nickel alloy, has no coefficient of expansion. *Platinite* (46 per cent of nickel) has the same coefficient of expansion as platinum. *High-speed steels* can be hardened and used for tools cutting at a high speed.

QUESTIONS

1. Why is a blast furnace kept in continuous operation?
2. What *four* materials must be supplied to a blast furnace?
3. What use has recently been found for slag?
4. Why is iron pyrite never put into a blast furnace?
5. Why are the chemical changes carried on in a Bessemer converter difficult to control?
6. Why is the air forced into a blast furnace dried and preheated?
7. What keeps the iron hot in a Bessemer converter?

8. Why is steel made by the open-hearth process generally superior to that made by the Bessemer process?

9. What kind of iron is used to make stoves? chains? hammers? chisels? bridges? safes?

10. What is the purpose of a " purifier " in making steel?

11. Which kind of steel is most easily welded? Why?

12. What is meant by the " critical range " of temperature in the heat treatment of steel?

13. Why is it more efficient to use " high-speed " tool steel than ordinary tool steel?

14. What determines the physical properties of steel besides its chemical composition?

15. Name four special steels and give two uses to which each is adapted.

16. What advantages has the electric furnace over other forms of furnaces for making steel?

TOPICS FOR FURTHER STUDY

Creators of the age of steel. What was the primitive method of obtaining iron from its ores? How was the metal made into tools? What have been the important modern inventions in the iron and steel industry? What men were closely connected with their development? Would our present civilization be possible without the blast furnace? (*Bird's* Modern Science Reader.)

Special steels, their uses and manufacture. What is meant by the " heat treatment " of steel? (*Slosson's* Creative Chemistry, *Bird's* Modern Science Reader, and *Spring's* Non-Technical Chats on Iron and Steel.)

CHAPTER XXXII

THE IRON FAMILY

Pure iron — iron chlorides — ferrous and ferric compounds — oxidation and reduction — hydroxides of iron — iron oxides — other iron compounds — ferrocyanides — ferricyanides — blue prints — inks.

Cobalt and nickel — properties and uses of the metals — typical compounds.

Having discussed the preparation, properties, and uses of iron and steel, we shall now consider iron as an element and shall describe some of its compounds. **Iron, cobalt,** and **nickel** are neighboring elements in the eighth group of the periodic system. They occur in the middle of the first long period and have metallic properties; but they differ from such elements as sodium and potassium in their relative inactivity and the fact that their hydroxides are weak bases.

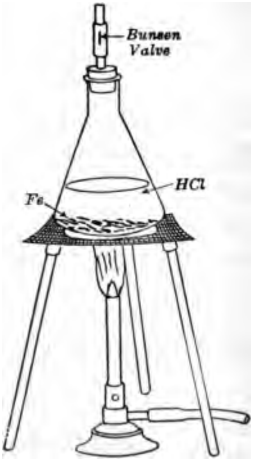

Fig. 233. Preparation of ferrous chloride.

409. Pure iron. Chemically pure iron can be made by the reduction of an iron salt with hydrogen. It has a white, metallic appearance and melts at about 1500° C. It is magnetic. Pure iron is not a very active metal and is not affected by cold water. It will decompose steam with the formation of iron oxide and hydrogen (§ 31). It readily displaces hydrogen from dilute acids (Fig. 233). If heated sufficiently it will burn in oxygen with the formation of the oxide (Fe_2O_3).

410. Iron chlorides. When iron is dissolved in hydrochloric acid in the absence of air, a compound called **ferrous chloride** ($FeCl_2$) is formed:

$$Fe + 2\ HCl \longrightarrow FeCl_2 + H_2\uparrow$$

The escaping gas generally has an offensive odor due to certain impurities in ordinary iron. Hot iron reacts with chlorine gas, forming scales of a dark brown solid known as **ferric chloride** ($FeCl_3$). The same compound is formed in solution when iron is dissolved in aqua regia. Both chlorides of iron are soluble in water and are used in the laboratory.

411. Ferrous and ferric compounds. Iron is an element which easily forms two series of compounds; in one of these it has a valence of **two** and in the other a valence of **three.** *Compounds in which iron is divalent are called **ferrous compounds** and those in which it is trivalent are called **ferric compounds**.* The chlorides just mentioned are typical examples of these two series of salts. Ferrous chloride in water gives the ferrous ion (Fe^{++}), and ferric chloride the ferric ion (Fe^{+++}).

Ferrous and ferric compounds may very readily be transformed into each other. If we treat ferrous chloride with a solution of chlorine water it is turned into ferric chloride according to the equation

$$2\ FeCl_2 + Cl_2 \longrightarrow 2\ FeCl_3$$

On the other hand, if we boil ferric chloride solution with iron filings ferrous chloride is formed:

$$2\ FeCl_3 + Fe \longrightarrow 3\ FeCl_2$$

412. Oxidation and reduction. The change from ferrous to ferric compounds is called **oxidation.** The reverse change is called **reduction.** We have previously used these two words only when oxygen was involved in a reaction, but we shall now see that their meaning can be amplified. When carbon monoxide burns it takes up one more atom of oxygen, *increasing* *its valence from two to four. This is an oxidation reaction.* Carbon is the positive element in carbon monoxide, and *any increase in the valence of a positive element is* ***oxidation****; any decrease in the valence of such an element is* ***reduction****.* It is not necessary that oxygen be the negative element which is added to the compound in order to increase its valence. In the case of iron chloride the addition of one chlorine atom to ferrous chloride produces ferric chloride; and this reaction is *exactly parallel to the addition of an oxygen atom to carbon monoxide: it is oxidation.* It will be well to bear in mind this new definition of oxidation and reduction.

While the oxidation and reduction of iron compounds can take place without the action of oxygen, it often happens that we employ oxygen indirectly for this purpose. For example, *hydrogen peroxide* will quickly *oxidize* a hydrochloric acid solution of ferrous chloride to ferric chloride:

$$2\,FeCl_2 + 2\,HCl + \underset{(H_2O_2)}{[O]} \longrightarrow 2\,FeCl_3 + H_2O$$

Hydrogen sulfide will *reduce* ferric chloride to ferrous chloride: the hydrogen takes chlorine from the ferric chloride and leaves sulfur free:

$$2\,FeCl_3 + H_2S \longrightarrow 2\,FeCl_2 + 2\,HCl + S\downarrow$$

413. Iron hydroxides. The addition of a base to a solution of a ferric salt gives a reddish brown precipitate of **ferric hydroxide**:

$$FeCl_3 + 3\,NaOH \longrightarrow Fe(OH)_3\downarrow + 3\,NaCl$$

Ferrous hydroxide ($Fe(OH)_2$) can be similarly precipitated from a ferrous salt. It is a white substance which is quickly oxidized by the air, turns green and finally brown, and becomes ferric hydroxide.

When ferric hydroxide is heated to a red heat it is converted into **ferric oxide** and water:

$$2\,Fe(OH)_3 \longrightarrow Fe_2O_3 + 3\,H_2O$$

Rust is the material which forms on the surface of iron when it is exposed to moist air. It is probably a mixture of ferric oxide and hydroxide. Its formation is hastened by the presence in the air of carbonic acid and other acid substances which help to dissolve some of the iron. Unlike the oxide of aluminum, rust does not adhere to the metal but keeps peeling off, exposing new portions to the action. For this reason a piece of iron will eventually turn completely to rust. Different grades of iron and steel rust at very different rates, and several schemes have been developed for protecting the metal from this action. Oil is used to keep tools from rusting because, although oxygen penetrates the oil, *moisture does not.*

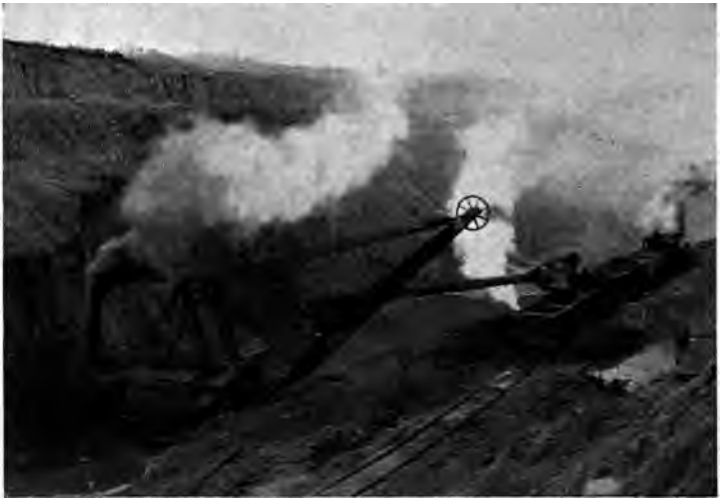

Fig. 234. Digging iron ore in Minnesota with a steam shovel.

414. Iron oxides. We have already seen that **ferric oxide** (Fe_2O_3) is the most important ore of iron. It occurs in great deposits, especially in northern Minnesota (Fig. 234). In the laboratory it can easily be prepared by heating ferric *hydroxide* or other ferric compounds. It is used as a coloring matter under the names of **Venetian red** and **Indian red.** One form of this oxide is known as **rouge**; it is used as a pigment and for polishing. Various hydrated ferric oxides are found naturally and are ores of iron. From them can be prepared pigments of different shades of yellow, orange, and brown. These are known as **sienna, burnt sienna,** and **umber.**

Magnetic oxide of iron (Fe_3O_4) also occurs naturally. It is found in the form of a mineral known as magnetite or **lodestone,** which has magnetic properties. This is the oxide which is produced when steam acts on hot iron. It is a black material and can be made in such a way that it will firmly adhere to iron. A film of this oxide prevents rusting, and iron thus coated is known as Russia iron. It is used for locomotive boilers.

415. Other iron compounds. **Ferrous sulfide** (FeS) is formed when ammonium sulfide ($(NH_4)_2S$) is added to a ferrous salt. It is a black insoluble compound. It is often used as a source of hydrogen sulfide. Another sulfide of iron is called **iron pyrite** (fool's gold) and has the formula FeS_2; it occurs abundantly in nature. It is sometimes used as a source of sulfur dioxide since when it burns it forms sulfur dioxide and iron oxide.

Ferrous sulfate ($Fe_2SO_4 \cdot 7\,H_2O$), called **green vitriol** or **copperas,** is a common compound of iron and is often used in the industries and the laboratory when a soluble iron compound is desired.

Ferrocyanides. Potassium ferrocyanide ($K_4Fe(CN)_6$) is a complex compound which is formed by igniting a mixture of nitrogenous organic material, potassium carbonate, and scrap iron and extracting the mass with hot water. It forms large yellow crystals, whence it is often called "yellow prussiate of potash."

In this compound the iron is bound to the carbon and nitrogen atoms, thus forming a negative radical. *A water solution of potassium ferrocyanide gives practically no iron ions.* It gives only potassium ions (K^+) and a complex tetravalent ion which is called the ferrocyanide ion ($Fe(CN)_6^{----}$). When potassium ferrocyanide and a ferric salt are brought together, a deep blue precipitate called **Prussian blue** is formed. This compound is **ferric ferrocyanide**:

$$4\,FeCl_3 + 3\,K_4Fe(CN)_6 \longrightarrow Fe_4(Fe(CN)_6)_3\downarrow + 12\,KCl$$

Prussian blue is used as a pigment and sometimes for the preparation of laundry bluing. If the fabrics which are dipped into this bluing are not free from soap and alkali, ferric hydroxide may be formed on the cloth, producing spots of iron rust.

Ferricyanides. By treating a water solution of potassium ferrocyanide with chlorine we get by evaporation garnet-red crystals of potassium ferricyanide ($K_3Fe(CN)_6$):

$$2\ K_4Fe(CN)_6 + Cl_2 \longrightarrow 2\ KCl + 2\ K_3Fe(CN)_6$$

Potassium ferricyanide is called "red prussiate of potash" and in solution gives the trivalent ion $Fe(CN)_6^{---}$. The difference between the formulas for potassium ferrocyanide and ferricyanide can be remembered by noting that in each compound there are six (CN) groups which require enough metallic elements to make up a valence of six. In the *ferricyanide, iron is trivalent; in the ferrocyanide, divalent.*

Ferrous salts give with potassium ferricyanide a dark blue precipitate of ferrous ferricyanide (Turnbull's blue):

$$3\ FeCl_2 + 2\ K_3Fe(CN)_6 \longrightarrow 6\ KCl + Fe_3(Fe(CN)_6)_2$$

We can test for a ferrous ion by using potassium ferricyanide; and for a ferric compound by using potassium ferrocyanide; in both cases we obtain a blue precipitate. These two tests are frequently applied in distinguishing between ferrous and ferric salts. We do not obtain a dark-blue precipitate with ferric salt and ferricyanide, or with ferrous salt and ferrocyanide.

416. Blue prints. The action of light will reduce the ferric salts of certain complex organic acids to ferrous salts. This reaction is taken advantage of in making **blue prints.** Paper can be treated with a ferric salt (ferric oxalate) in the dark and dried. It can then be exposed to light under a photographic negative or an ink drawing on tracing cloth. Where the light strikes the paper the ferric compounds will be reduced to ferrous, and the amount of reduction will be in proportion to the amount of light that reaches the paper. After exposure the paper can be dipped into a solution of potassium ferricyanide, and wherever ferrous compounds have been produced Turnbull's blue will be formed. Where the paper has been protected from the light there will be no action, and the unchanged ferric salt will be washed away. There is thus left a blue and white picture called a **blue print**.

Commercial blue-print paper is coated with a mixture of ammonium ferric citrate and potassium ferricyanide. The ammonium ferric citrate is the best ferric salt for the purpose. The developer, potassium ferricyanide, is put directly on the paper in the first place. After exposure to light such a paper is dipped into water, and the blue color is formed at once. It is then washed with water until all the unchanged chemicals have been removed; the print is now permanent.

417. Inks. An organic compound called **tannic acid** is obtained from certain vegetable products (*nutgalls*). With ferric salts this substance forms a jet-black, insoluble **ferric tannate.** A number of years ago a colloidal solution of this material in water was used as a **writing ink.** A better ink was later prepared by mixing a slightly acid solution of ferrous sulfate and tannic acid. *Ferrous tannate* is soluble and colorless, and no black color is produced until the mixture is exposed to air. To make the ink visible a blue dye is added; the writing slowly turns black as the ferrous salt is oxidized and ferric tannate is produced. This is the so-called **blue-black ink.** Ferric tannate is particularly suitable as a writing fluid because it is very permanent.

418. Ink spots and other stains. Ink spots which are fresh can generally be removed by simply washing with water, in which all the ingredients are soluble. After standing for some time, however, the ink spot contains the insoluble ferric tannate. Such a spot can be removed by treating it with a reducing agent which will reduce the ferric salts to ferrous. Ammonium oxalate or a dilute solution of oxalic acid is suitable for this purpose. Lemon juice contains an organic acid (citric acid) which is a reducing agent, and ink spots are often removed in the household by the use of lemon.

Rust stains are often rendered soluble by the same treatment as that used for ink spots. **Coffee and tea stains** can be washed out of cotton or wool *by boiling water if it is applied at once*. Stains on silk can seldom be entirely removed; hypochlorous acid (§ 336) should never be used on them.

Water will take out **sugar** and **sirup** stains. But for **grease** it is necessary to use some other solvent, such as carbon tetrachloride or gasolene, and to absorb the solution with blotting paper or clean white cloth to prevent its spreading.

COBALT AND NICKEL

419. Properties and uses of the metals. These elements, like iron, form two series of salts in which the metals are divalent and trivalent respectively. Aside from their use in alloys, the elements are relatively of little importance. Both metals are, like iron, magnetic.

Nickel is a white, hard, malleable metal which can be highly polished. As this polish is not affected by moist air, a great many objects are plated with a thin coating of nickel, which gives them a pleasant appearance and prevents their corrosion. The nickel is plated on by means of an electric current.

Nickel is a component of a number of alloys. **Monel metal** contains approximately equal parts of copper and nickel; it is made by the smelting of a natural ore in which nickel and copper occur in these proportions. This alloy is used for modern rifle bullets, which are as hard as steel and much heavier. It is stronger than ordinary steel and has valuable acid-resisting properties. **Nickel steel,** containing about 5 per cent of nickel, is both hard and tough; hence armor plates for battleships are made of it. **Nickel for coinage** is made of three parts of copper and one of nickel. **German silver** contains copper, zinc, and nickel. All of these alloys find certain special uses because of their resistance to corrosion by moist air and chemicals.

Cobalt is a metal which closely resembles nickel. It is used for making a few special alloys. As there is no extensive commercial use for pure cobalt, the metal is not extracted on a large scale.

420. Typical compounds. The compounds of nickel and cobalt which are most extensively used are the cobaltous and nickelous compounds, such as cobaltous chloride ($CoCl_2$) and nickelous sulfate ($NiSO_4$). Nickel carbonyl ($Ni(CO)_4$) is a rather interesting and somewhat important substance: the **Mond process** for separating nickel from copper depends on the formation of nickel carbonyl and its subsequent decomposition into pure nickel. It is a volatile, colorless liquid which is formed by passing carbon monoxide over warm, finely divided nickel. On heating to 180° C. it is decomposed into nickel and carbon monoxide.

SUMMARY OF CHAPTER XXXII

IRON, NICKEL, AND COBALT are neighboring elements in the eighth group.

PURE IRON is not affected by cold water but when heated will decompose steam. It will burn in oxygen if heated sufficiently hot. Iron forms two series of compounds, the *ferrous*, in which iron is *divalent*, and the *ferric*, in which it is *trivalent*.

Ferrous compounds may be *oxidized* to ferric compounds, and the latter *reduced* to ferrous. *Oxidation* is a reaction which increases the valence of the positive element in a molecule; *reduction* decreases it.

***Ferric hydroxide and ferrous hydroxide* are insoluble substances. *Rust* is a mixture of ferric oxide and hydroxide. It is formed by the action of moist air on iron; it peels off and hence does not protect the iron.**

IRON FORMS THE OXIDES FeO, Fe_2O_3, and Fe_3O_4. The latter can be formed as an adhering coating on iron by the action of steam. Such iron is called Russia iron.

***Potassium ferrocyanide* forms Prussian blue with a ferric salt. Prussian blue is used as a pigment and in making bluing.**

***Potassium ferricyanide* gives a precipitate of Turnbull's blue**

with a ferrous salt. A ferrocyanide is a test for a ferric salt, and a ferricyanide for a ferrous salt.

BLUE PRINTS are made on paper coated with a reduceable ferric salt and potassium ferricyanide. The ferric salt is reduced by light to ferrous. On being treated with water the potassium ferricyanide and ferrous salt combine, forming Turnbull's blue; the unchanged chemicals are washed away.

BLACK INKS are made from ferric tannate, a black, insoluble material. Blue-black inks contain ferrous tannate, which slowly oxidizes in the air to ferric tannate.

COBALT AND NICKEL are both magnetic like iron. Metals are often coated with a film of nickel because it is not affected by air and because it takes a polish. Monel metal and German silver are alloys of nickel.

QUESTIONS

1. How does paint protect iron from rusting?

2. Compare the rusting of iron with the " rusting " of aluminum.

3. Why are the ferric compounds more stable than the ferrous?

4. Explain the fact that a solution of sodium carbonate precipitates the hydroxide and not the carbonate from a solution of a ferric salt.

5. Will ammonium hydroxide precipitate the iron hydroxide from a solution of any iron compound?

6. Write the equations for producing nascent hydrogen and using it to reduce ferric chloride.

7. What other oxidizing agents besides hydrogen peroxide might be used to change ferrous compounds to ferric?

8. How would you prove that a given solution contained *both* ferrous and ferric salts?

9. Why do the stains made by iron inks gradually become brown?

10. What properties have cobalt and nickel in common with iron?

11. Why is iron copper plated before it is nickel plated?

12. Name and give the uses for four nickel alloys.

13. What is the composition of Turnbull's blue? How is it prepared?

14. What precautions must be taken when Prussian blue is used for laundry purposes?

15. For what special purposes are blue prints adapted?

CHAPTER XXXIII

ZINC, TIN, AND LEAD

Metallurgy in general — zinc ores — zinc oxide and hydroxide — chloride — sulfide, its precipitation.

Metallurgy of tin — tin plate — stannous and stannic salts — chlorides — stannic acid — mordants — recovery of tin from tin plate.

Metallurgy of lead — lead alloys — lead oxides — lead storage battery — white lead.

Replacement series of metals — corrosion of iron.

421. General principles of metallurgy. A few metals, such as copper, silver, and gold, occur free in nature, and their manufacture into articles of commerce is, of course, comparatively simple. For the most part, however, the important metals are found as compounds containing sulfur, oxygen, and silicon. Many compounds of the metals which occur naturally as minerals are not suitable for use in the preparation of the free metals. In general, *the oxides, sulfides, and carbonates*, when they are mined in a comparatively pure condition, *are the most suitable starting points.* Such substances are called **ores**, and the science that deals with the extraction of metals from their ores is called **metallurgy.**

We have already learned that the *active metals*, like sodium, aluminum, and calcium, can be obtained only by the *electrolysis of their fused salts.* This is a general method of obtaining the active metals. But before such a process can be carried out pure salts of the elements must be obtained; for this reason and because large electric currents are required, the process is relatively difficult and expensive. In the production of iron from its ores we met with a simpler process of extraction. In this case *the ore (an oxide) was reduced to the free metal by the very cheap substance carbon* (or carbon monoxide). The metallurgy of iron is a good example of the general method of obtaining the less active metals from their ores. By heating the oxide of many metals with carbon or with carbon monoxide the free metal is obtained. When the ore is a sulfide it must first be heated in the air (roasted) in order to be converted into the oxide.

If ores contained only the pure oxide or sulfide, metallurgy would be a much simpler art. But, as we saw in the case of iron, they are always contaminated with more or less other mineral material. This is called **gangue** and usually consists of calcium or magnesium silicates, calcium carbonate, or free silica. The removal of the gangue is accomplished by using as a **flux** some material which will combine with it at a high temperature to form a fusible, glass-like material. The latter floats on the metal and is called **slag**. If the gangue is essentially an acid anhydride, like silicon dioxide, we add either lime or limestone; if the gangue is calcium carbonate (which goes into the oxide on heating), we add silica as a flux. In both cases *the slag is essentially calcium silicate.*

By bearing these general principles in mind we can more easily correlate and remember the metallurgy of the common metals.

ZINC

422. Metallurgy. The metallurgy of zinc is simple. The principal ores are the oxide called **zincite** (ZnO) and the sulfide called **zinc blende** (ZnS). The sulfide on roasting produces the oxide. The oxide is mixed with finely powdered coal and heated in earthenware retorts in order to reduce it to metallic zinc:

$$ZnO + C \longrightarrow Zn + CO$$

The retorts are heated above the boiling point of the metal (950° C.), which passes off as a gas and is condensed to a liquid in earthenware or iron receivers. The molten metal is then run into molds and allowed to solidify.

423. Properties and uses. Zinc is a bluish white metal and as it ordinarily comes from the smelter is rather crystalline and brittle. At a temperature of about 100° C. it is malleable and ductile and can be rolled into sheets.

It is a constituent of a number of alloys, such as **brass** (copper and zinc), **German silver** (copper, nickel, and zinc), and **bronze** (copper, tin, and zinc). The metal has a limited application; it is used, for instance, as the negative plate of all electric batteries except storage batteries. **Galvanized iron** is iron covered with a thin layer of zinc. This is done by dipping the metal into molten zinc, or by a process of electroplating.

Compounds of Zinc

424. Zinc oxide and hydroxide. When zinc is heated sufficiently hot it takes fire in the air, forming the *white oxide* (ZnO). The same oxide may be prepared by heating the hydroxide or zinc carbonate. Zinc oxide is used to make zinc ointment; also as a white pigment (**zinc white**) in the manufacture of paint; and very extensively as a filler in the manufacture of white rubber. **Zinc hydroxide** ($Zn(OH)_2$) is precipitated when sodium hydroxide is added to a zinc salt. Zinc hydroxide, like aluminum hydroxide, will dissolve in either acids or bases.

425. Zinc choride. This salt ($ZnCl_2$) is obtained by dissolving zinc in hydrochloric acid. When it is evaporated it gives a white solid which rapidly absorbs water from the air; for this reason it is sometimes used as a drying agent. Solutions of zinc chloride will dissolve oxides of many metals and are therefore valuable for cleaning the surfaces of metals before soldering. Wooden posts and railroad ties which are impregnated with it are much more resistant to the action of decay and disintegration; hence considerable quantities of the salt are applied to this purpose.

Zinc sulfate ($ZnSO_4$) is another common salt of zinc which is soluble in water; it forms transparent crystals ($ZnSO_4 \cdot 7\ H_2O$) which are called **white vitriol.**

426. Zinc sulfide. This compound (ZnS) can be prepared by the direct combination of zinc dust and sulfur, or by passing hydrogen sulfide into a solution of certain zinc salts.

Zinc sulfide is a white solid which is insoluble in water. When mixed with barium sulfate it is called **lithophone** and is extensively used as a white pigment. The action of the barium sulfide on the zinc sulfate is as follows:

$$ZnSO_4 + BaS \longrightarrow ZnS + BaSO_4$$

427. Precipitation of zinc sulfide. Zinc sulfide is readily soluble in moderately dilute hydrochloric acid; hydrogen sulfide and zinc chloride are formed:

$$ZnS + 2\ HCl \longrightarrow ZnCl_2 + H_2S$$

When hydrogen sulfide is passed into zinc chloride solution, only a small part of the zinc is precipitated because this is a reversible reaction:

$$ZnCl_2 + H_2S \rightleftharpoons ZnS + 2\ HCl$$

The condition of equilibrium will depend on the concentration of the acid (the concentration of the hydrogen ion) which is present. If we acidify a solution of zinc chloride, we cannot precipitate any zinc sulfide from it with hydrogen sulfide. If instead of hydrogen sulfide we use ammonium sulfide ($(NH_4)_2S$), we can precipitate zinc sulfide completely, as the solution is now neutral:

$$ZnCl_2 + (NH_4)_2S \longrightarrow ZnS \downarrow + 2\ NH_4Cl$$

TIN

428. Metallurgy. Tin oxide (SnO_2) is the only important ore. The metal is produced by heating the oxide with carbon in a reverberatory furnace:

$$SnO_2 + C \longrightarrow Sn + CO_2$$

The molten metal which collects at the bottom of the furnace is drawn off and cast into ingots. These are afterwards remelted at a gentle heat, and the pure metal flows away from the impurities.

429. Tin plate. Tin is a white metal, soft and malleable. Pure tin is known ordinarily as **block tin.** It is very resistant to ordinary atmospheric corrosion and for this reason is widely used as the protective coating on other metals. Ordinary **tinware** (tin plate) is sheet iron or steel which has been coated with a thin layer of metallic tin by being dipped into the molten metal. This material is often erroneously called simply " tin."

Tin foil is tin hammered or rolled into thin sheets; most tin foil, however, contains considerable lead. Tin is used in making many alloys, which have already been considered.

COMPOUNDS OF TIN

430. Stannous and stannic salts. Tin forms two series of compounds in which it has the valence of two and four respectively. These are called **stannous** and **stannic salts.** Stannous compounds have a very decided tendency to go over into stannic compounds and for this reason are strong reducing agents. For example, ferric chloride is reduced by stannous chloride:

$$2\,FeCl_3 + SnCl_2 \longrightarrow 2\,FeCl_2 + SnCl_4$$

431. The chlorides and stannic acid. Tin will dissolve in hot concentrated hydrochloric acid, producing **stannous chloride** ($SnCl_2$). The salt crystallizes with two molecules of water ($SnCl_2 \cdot 2\,H_2O$). **Stannous hydroxide** ($Sn(OH)_2$) is precipitated as a flocculent white precipitate when a soluble base is added to stannous chloride solution.

Stannic chloride ($SnCl_4$) is formed by the oxidation of stannous chloride, or by the direct action of metallic tin and chlorine. Stannic chloride differs considerably from the salts of most metals in that it is a colorless liquid which fumes in moist air. With water it forms a number of crystallized hydrates. **Stannic hydroxide** is precipitated when sodium hydroxide is added to a solution of stannic chloride:

$$SnCl_4 + 4\ NaOH \longrightarrow Sn(OH)_4 + 4\ NaCl$$

This hydroxide has properties more definitely acidic than basic and is therefore sometimes called **stannic acid**. It readily dissolves in an excess of sodium hydroxide, forming sodium stannate:

$$Sn(OH)_4 + 2\ NaOH \longrightarrow Na_2SnO_3 + 3\ H_2O$$

Stannic acid in the form of its salts is extensively used in the preparation of silk goods. Silk cloth is treated with a solution of a tin salt and then with sodium hydroxide. The cloth becomes impregnated with stannic hydroxide, which is distributed through the finished fiber in some sort of solid colloidal solution and gives to the goods the desired weight and finish. Cotton goods are rendered noninflammable by a similar treatment. The amount of stannic acid which both cotton and silk can take up and hold is very surprising. Silk often contains as much as twice its own weight of metallic tin in the form of stannic acid.

432. Mordants. This ability of fabrics to hold the hydroxides of metals like tin is of great importance in the dyeing industry. Many dyes which are extensively used are not readily absorbed by fabrics and under ordinary conditions will either not dye the cloth at all or can easily be washed out. A number of them will, however, form insoluble, colored, complex compounds with the hydroxides of many metals. These compounds are called **lakes** and are used to a certain extent in the manufacture of special paints. If the hydroxide is precipitated on the cloth in the presence of the dye, it will bind the colored material to the fabric. The metallic salts which yield such hydroxides are called **mordants**. A mordant, therefore, is a substance which will combine with a dye to form a colored compound and which is also held firmly by the fabric. In other words, a *mordant serves as an anchor between the dye and the cloth.* Aluminum hydroxide, iron hydroxide, stannous hydroxide, and stannic hydroxide are common mordants. The cloth is first treated with the salt of the metal, then with the dye, and finally steamed; the steam causes the hydrolysis of the salt, and the hydroxide is precipitated. Tannic acid is also a mordant and is used for those dyes which will not combine with basic substances but which require some acidic material.

433. Recovery of tin from tin plate. Great quantities of tin enter into the manufacture of tin plate. This tin plate is used in the manufacture of tin cans and similar objects which are soon discarded and which find their way to the junk heap. The tin can be recovered from such material by treating it with chlorine at a certain temperature. Stannic chloride is formed, which can be distilled away from the other metals and obtained pure. It is then used as a source of stannic hydroxide for the textile industries.

LEAD

434. Metallurgy. The commonest ore of lead is **galena**, which is the sulfide (PbS). There are two methods of extracting lead from its ores: one is carried out in a reverberatory furnace and the other involves the use of a blast furnace. The latter process is now most widely employed.

This blast furnace is much like an iron furnace, except that it is shorter and wider. The charge consists of ore which has first been roasted in an open-grate furnace. The roasting *partially* converts the ore into oxide. The other materials in the charge are coke and a flux consisting of a mixture of iron oxide and limestone; the gangue is usually quartz. The combustion of the coke furnishes the necessary heat, and the lead oxide is reduced by the carbon monoxide and the carbon; some iron is also formed by the reduction of the iron oxide. This iron in turn reacts with the lead sulfide, forming iron sulfide and lead:

$$PbS + Fe \longrightarrow FeS + Pb$$

Metallic lead and a slag form the two layers at the bottom of the furnace and are drawn off.

Lead ores usually contain gold and silver, which are found in the crude metal. As molten lead is an excellent solvent for these precious metals, materials which contain a small amount of them are chosen for the flux. In this way the process does two things at the same time: it produces lead and extracts the precious metals from very poor ores.

Lead obtained in this way contains a number of impurities which make it hard. In order to get soft lead these must be removed. This is done by heating the metal in a reverberatory furnace at a low temperature. A scum containing most of the impurities is formed and is skimmed off. Silver is removed by the Parke process, which we shall consider later.

435. Properties, uses, and alloys. Lead is a soft, white metal with a brilliant luster when freshly cut. It is oxidized by the air, producing a thin adhering film, which protects it. Because it is easily cut and bent, and because its edges may be readily fused or soldered, lead is made into pipes and sheathing for cables. It can also be rolled into thin sheets and used as lining for tanks, electrolytic cells, and similar objects.

Lead is a low-melting metal and is a component of a number of low-melting alloys, such as **type metal** (lead, tin, and antimony), **solder** (lead and tin), and **lead shot** (containing either arsenic or antimony).

COMPOUNDS OF LEAD

The common compounds of lead are those in which the element is divalent and gives the ion Pb^{++}. Lead also forms a few compounds in which it is tetravalent, but these compounds are of less importance.

436. Lead oxides. Litharge (PbO), a yellow oxide of lead, is made by heating lead in air. It is very widely used in the preparation of paints and varnishes and in the manufacture of other lead compounds. A mixture of litharge and glycerin sets to a very hard mass and makes a valuable cement for laboratory purposes.

Another oxide of lead can be formed by heating metallic lead or litharge in the air at just the right temperature (about 400° C.). This is a red substance known as **red lead**, or **minium** (Pb_3O_4). It is put into paints as a pigment; it is also one of the substances which accelerate the drying of linseed oil. A paint made of it is very largely used on iron work as it makes a satisfactory coating and is cheap.

Lead dioxide (PbO_2) is a brown powder made by treating red lead with nitric acid. It is a strong oxidizing agent.

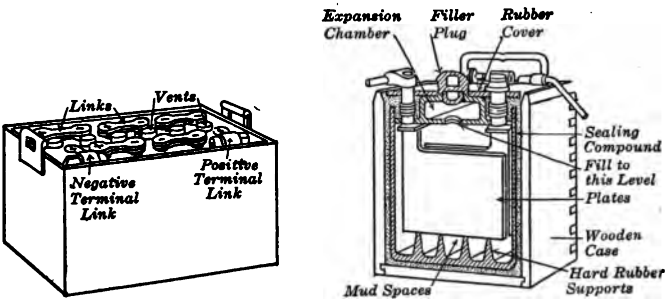

Fig. 235. Lead storage battery used on automobiles for starting and lighting.

437. Lead storage battery. The storage battery has come to be an essential part of the lighting and starting equipment of an automobile. It is also an important part of the reserve equipment of electric-power stations. *It is not an apparatus for storing up electricity which is to be drawn out at some future time*, but it is a device by which electrical energy is used to produce a chemical reaction; when this chemical action is reversed the cell delivers current. Thus the electrical energy is transformed into chemical energy in charging, and this in turn can be converted back again into electrical energy in discharging.

The usual automobile battery (Fig. 235) comprises either three cells (6 volts) or six (12 volts). Each cell contains lead plates dipping into dilute sulfuric acid. One set of plates, called the **negative** (−), is *gray* in color and contains pure, finely divided lead. The other set of plates, called the **positive** (+), is *dark brown* in color and is coated with lead dioxide (PbO_2). All the negative plates of one cell are joined to one another, and the positive plates are likewise connected. The two sets are sandwiched together with perforated insulators between. There is always one more negative plate than there are positive plates in each cell.

The reversible reaction which takes place in charging and discharging is as follows:

$$Pb + PbO_2 + 2\,H_2SO_4 \underset{\longleftarrow \text{ Charge}}{\overset{\text{Discharge} \longrightarrow}{\rightleftharpoons}} 2\,PbSO_4 + 2\,H_2O$$

In discharging, the two plates come to the same condition ($PbSO_4$), and the acid is made more dilute by the formation of water. In practice the *cell is never allowed to become completely discharged.* In charging, the positive electrode (+) is attached to the positive terminal of a direct-current generator, the plates are restored to their original condition, and the acid becomes more concentrated.

438. White lead. One of the commonest pigments used in oil paints is **white lead** ($Pb(OH)_2 \cdot 2\,PbCO_3$). This substance is essentially a mixture of lead hydroxide and lead carbonate (called a basic carbonate). It is a heavy, white, insoluble substance which when mixed with linseed oil forms a white paint with great covering power. It is often taken as the body in making colored paints, certain other pigments being added to give the required color. The disadvantage in using white lead is that it turns black when it comes in contact with hydrogen sulfide, owing to the formation of black **lead sulfide** (PbS). Hydrogen sulfide is always present in small amounts in city air, and for this reason white paint often turns black. Zinc oxide, zinc sulfide, and lithophone are superior to white lead in this respect. White pigments containing zinc will not blacken because zinc sulfide itself is white. Zinc paints, however, are more expensive than white lead, which is still used in enormous quantities in the paint industry.

White lead can be manufactured by a number of different processes, all of which depend on the action of water, air, and carbon dioxide on *metallic lead in* the presence of a weak acid like acetic acid. The old

Dutch process, which is still used, gives a very fine product. Gratings of lead called " buckles " are put in pots, as shown in figure 236. In the bottom of the pots is placed dilute acetic acid (vinegar). They are then buried in a mass of moist tanbark or manure. The decomposition of the organic material in the manure or bark produces carbon dioxide and moisture; heat is also given off. The vapors of the dilute acetic acid attack the warm lead, forming lead acetate. The carbon dioxide and water react with this and produce white lead. After three or four months the lead is completely corroded and in its place is a mass of white lead. The pigment is now separated from any unchanged lead, is ground, and passed through sieves. It is finally ground in linseed oil and is sold as a thick paste. Several newer processes are now used for carrying out the same reaction in a shorter time.

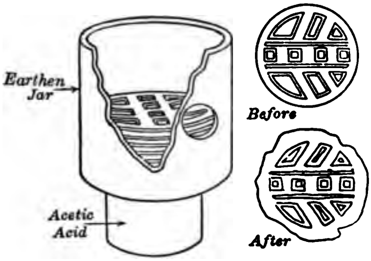

Fig. 236. White-lead buckles and earthen pot.

Another pigment, **chrome yellow**, which may be mentioned at this point, is lead chromate ($PbCrO_4$). This is formed by adding potassium chromate (K_2CrO_4) to a soluble lead salt.

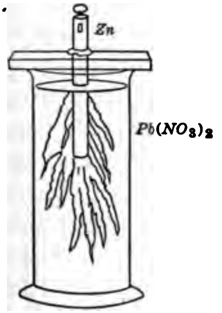

Fig. 237. Lead tree.

439. The replacement series of metals. We have already seen that metallic zinc can replace the hydrogen ion from an acid solution and set free hydrogen gas, and that in the case of the halogens there is a definite order in which one element can replace another from a solution. Such a series for the metals is shown below. For example, a strip of zinc placed in a solution containing the salt of any other metal below it in the series will form a zinc salt and precipitate the corresponding metal. Figure 237 shows zinc replacing lead in a solution of lead nitrate. The reaction is as follows:

$$Zn + Pb(NO_3)_2 \longrightarrow Zn(NO_3)_2 + Pb$$

or

$$Zn + Pb^{++} \longrightarrow Zn^{++} + Pb$$

It should be noticed that hydrogen is given a place in the series because, like the metals, it forms a positive ion. Any metal above hydrogen can replace this element from an acid; for example, zinc and dilute sulfuric acid:

$$Zn + H_2SO_4 \longrightarrow ZnSO_4 + H_2$$

or

$$Zn + 2\,H^+ \longrightarrow Zn^{++} + H_2$$

Elements below hydrogen do not liberate hydrogen when brought into contact with acids. The higher members of the series are so active that they decompose water. That is, they replace the hydrogen from water, which gives only a very minute concentration of hydrogen ions. The metals below aluminum have no appreciable action with hot or cold water and are therefore considered as *relatively inactive metals.*

REPLACEMENT SERIES OF METALS

Potassium
Sodium
Calcium
Magnesium
Aluminum
Zinc
Iron
Tin
Lead
Hydrogen
Copper
Mercury
Silver
Platinum
Gold

440. The corrosion of iron. We can now apply what we have just learned to a consideration of an important industrial problem, namely, the corrosion of iron. Absolutely pure iron is attacked only very slowly by dilute acids and therefore very slowly by the atmosphere. Impurities in it tend to set up tiny electric cells which greatly hasten the solution of the iron. For this reason impure metals often corrode faster than very pure ones. *There are three general methods of preventing the corrosion of iron:*

In the *first* method we merely cover the iron with some sort of resisting paint which will adhere to it and as completely as possible *shut out air,* carbon dioxide, and water. A similar method substitutes for the paint a thin coating of some fusible silicate; various grades of enamel ware are made in this way.

The *second* method consists of coating the iron with an element like zinc (galvanized iron) which stands above it in the replacement series. At first sight it seems rather remarkable that a more active metal should be able to protect iron from corrosion. Since the zinc is more active than the iron, it goes into solution, and hydrogen comes out of solution on the iron surface, which is not attacked. As long as any zinc coating is left it will go into solution instead of the iron. In this way the iron is protected.

The *third* method of protecting iron involves coating it with some less active metal like tin (tin plate). In this case we depend on the inactivity of tin to prevent any corrosion at all; *this is satisfactory as long as the tin coating is perfect.* If corrosion starts, both the iron and the tin come into contact with slightly acid solutions, and the very worst possible conditions are at hand. Iron being more active than tin goes into solution, and hydrogen is deposited on the tin, which is not changed. Therefore, as soon as tin plate begins to corrode, it disintegrates more rapidly than pure iron.

SUMMARY OF CHAPTER XXXIII

ZINC is made by reducing the oxide with carbon and distilling off the metal. It is a component of brass and bronze. It is used in electric batteries and for coating iron (galvanized iron).

***Zinc oxide* is used in making zinc ointment and as a paint pigment. *Zinc hydroxide* acts as a base with strong acids and as an acid with strong bases. It dissolves in sodium hydroxide, forming *sodium zincate.* *Zinc chloride* is used to clean metals before soldering and as a wood preservative. *Zinc sulfide* is precipitated by ammonium sulfide. It is a white solid and is used as a white pigment.**

TIN is obtained by reducing the oxide with carbon. It is not corroded by the atmosphere and is used for coating iron.

It forms two sets of compounds: stannous (divalent) and stannic (tetravalent). *Stannous chloride* is made by the action of hydrochloric acid on tin. It is used as a reducing agent. *Stannic chloride* is a liquid, formed by the action of chlorine on tin. *Stannic hydroxide* is acidic and is often called *stannic acid.* It is absorbed by silk and cotton.

Hydroxides of tin, iron, and aluminum act as **mordants:** they anchor the dye to the cloth.

LEAD occurs chiefly as a sulfide. The ore is first roasted and then reduced in a blast furnace. It is used for piping, as a covering for cables, and in alloys, such as type metal, solder, and shot.

Lead forms the *oxides:* litharge, red lead, and lead dioxide. The first two are used in paints and the last is used in *storage batteries. White lead* is a basic carbonate of lead. *Chrome yellow* is lead chromate.

IN THE REPLACEMENT SERIES OF METALS the position of any metal depends upon its relative tendency to ionize. Any element will replace any other element that stands below it.

IN THE CORROSION OF GALVANIZED IRON the more active metal zinc goes into solution; in the case of tin plate the iron goes into solution. *Tin protects iron* only as long as the entire surface is covered.

QUESTIONS

1. Why are there so many electrochemical works located at Niagara?

2. Name two reducing agents commonly used in metallurgy.

3. Explain the meaning of these terms: *gangue*, *flux*, and *slag*.

4. What advantages as a paint has zinc white over white lead?

5. What use has a tinsmith for a solution of zinc chloride?

6. When zinc sulfate solution is tested with litmus, it shows an acid reaction. Explain.

7. How would you test for the presence of zinc?

8. What are the disadvantages in using tin plate for covering roofs?

9. What is the function of a mordant? Name three and give their formulas.

10. What is the formula for *minium? white lead? block tin? litharge?*

11. What advantages has lead for making water pipes? What disadvantages?

12. Why are pipes made of block tin commonly used in connections for soda-water fountains?

13. What is *galvanized iron?*

14. What is the function of red lead in paints and varnishes?

15. What is the change in the density of the electrolyte in a lead storage battery during discharge?

16. What is the equation for the chemical change involved in charging a lead storage cell?

17. Summarize the facts you have learned from studying the replacement series of metals.

18. Explain why iron when coated with zinc is protected more effectively than when coated with tin.

TOPIC FOR FURTHER STUDY

The corrosion of iron and steel. What are some of the modern methods of preventing corrosion? Special iron alloys (" Duriron " and " Buflokast " iron, for example) are very resistant to corrosion. What do they contain besides iron? (*Slosson's* Creative Chemistry.)

CHAPTER XXXIV

COPPER, MERCURY, AND SILVER

Metallurgy of copper — properties and uses — copper oxides and sulfate — electric cell.

Mercury — mercurous and mercuric chloride.

Metallurgy of silver — silver nitrate — silver halides — photography — separation of metals into groups.

441. Position in the replacement series. It will be noted that the metals zinc, tin, and lead come in the replacement series just *above* hydrogen. In this chapter we shall study copper, mercury, and silver, which come just *below* hydrogen. In the following chapter we shall consider platinum and gold, the lowest members of this series of metals. We shall also see that this replacement series has a very important meaning in electrochemistry.

COPPER

442. Metallurgy. Free copper is found in large quantities in the Lake Superior region. In order to isolate **native copper** it is necessary only to grind the rock to a powder and then to heat it until the metal runs together and flows to the bottom of the mass.

In Arizona copper is found as a basic carbonate called **malachite** ($Cu_2(OH)_2CO_3$) and in some places as the oxide **cuprite** (Cu_2O). The carbonate and oxide ores require only coal and heat to remove the oxygen.

In Montana (Fig. 238) and Utah the copper occurs as sulfides, **copper pyrite** ($CuFeS_2$) and **chalcocite** (Cu_2S). The extraction of copper from the sulfide ores is difficult and often requires very complicated methods of treatment. This is the case because the iron sulfide has to be separated from the copper by changing it first into an oxide (by roasting) and then into a silicate (with sand). The iron silicate forms a flux which separates from the molten copper and copper sulfide.

The *first* step, which consists in converting some of the sulfides to oxides, is carried out in a reverberatory furnace or a small blast furnace. The product of this melting is called the **matte**, and contains about 50 per cent copper. In the *second* step the molten matte is run into a small converter lined with sand. A blast of air is forced in below the surface of the molten mass; the sulfur is oxidized and passes off as sulfur dioxide, and the iron unites with the siliceous lining of the converter and forms a liquid slag. When the impurities are oxidized as far as possible, the slag is first run off, and then the melted copper is cast into plates, known as **anodes**, for electrolytic refining.

Fig. 238. Copper mining.

443. Low-grade copper ores. It has recently been found possible and practicable to utilize ore containing even so small an amount of copper as only 2 per cent. By means of the **froth flotation process** about 85 to 90 per cent of the copper is recovered. The ore is first crushed to a fine powder and then mixed with water containing some cheap oil and sometimes a little sulfuric acid. This mixture is stirred vigorously and then allowed to flow into a large tank of water. Here the rock material at once settles to the bottom, while the bits of ore are held in the oily froth which rises to the top.

444. Electrolytic refining. The copper obtained from the smelters always contains small amounts of other metals, including gold and silver. But even small amounts of impurities greatly impair the electrical conductivity of copper; therefore this metal must be further refined before being used.

This is done by a process of **electrolysis.** Thin strips of pure copper are made the cathode in a solution of copper sulfate ($CuSO_4$); thick plates of impure copper form the anode (Fig. 239). A current is passed through the cell, and electrolysis takes place. The current is carried through the solution by the copper ions (Cu^{++}), metallic copper is deposited at the cathode and dissolved at the anode. The copper thus obtained at the cathode is very pure (about 99.8 per cent); the impurities for the most part drop to the bottom of the tank and form what is known as the **anode slime.** The amount of gold and silver recovered from the slime is often sufficient to pay for this extra step in the refining of the copper.

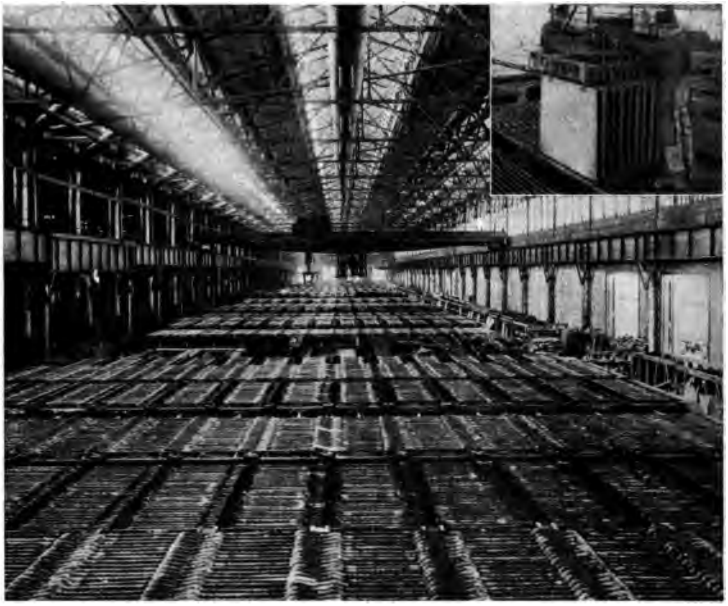

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Fig. 239. Electrolytic refining of copper.

445. Properties and uses. Copper is a malleable, ductile metal. It is the best conductor of electricity known, except silver. Copper is not affected by dry air but is slowly attacked under ordinary atmospheric conditions, forming a coating of a green basic carbonate. This coating is adherent and protects the metal from further action.

Copper in the form of wire, bars, etc., is very widely used as a conductor of electricity. Because of its resistance to corrosion, metal roofing for buildings and coverings for ships' bottoms are made of it.

Two widely used alloys of this metal are **brass**, an alloy of copper and zinc, and **bronze**, an alloy of copper and tin. **Phosphor bronze** contains in addition to these metals one to four per cent of phosphorus, which is present as the phosphide of one of the metals. It is a hard alloy not easily corroded and is used for making such things as ships' propellers and shafting.

COMPOUNDS OF COPPER

446. Two series of copper compounds. Copper is like iron in that it forms two sets of compounds: the **cuprous** compounds, in which it is monovalent; and the **cupric** compounds, in which it is divalent. Most of the common compounds are cupric salts.

447. Oxides of copper. The most important cuprous compound is the red oxide of copper, **cuprous oxide** (Cu_2O), which is formed in testing for glucose by means of **Fehling's solution.** This solution contains copper sulfate ($CuSO_4$), potassium hydroxide, and Rochelle salt ($NaKC_4H_4O_6 \cdot 4\,H_2O$). When glucose is added to it and the mixture is boiled, cuprous oxide separates as a red precipitate.

Black oxide of copper, **cupric oxide** (CuO), can be made by heating copper in air and also by heating cupric hydroxide, nitrate, or carbonate:

$$Cu(OH)_2 \longrightarrow CuO + H_2O$$

448. Cupric sulfate, or blue vitriol ($CuSO_4 \cdot 5\,H_2O$). The hydrated sulfate of copper, or **bluestone**, is the most important of all the compounds of copper. It forms large blue crystals. It is used in gravity cells (Fig. 240), in copper plating, and in electrotyping. A mixture of copper sulfate and slaked lime, known as **Bordeaux mixture**, is employed as a fungicide to spray fruit trees, grapevines, and potato plants (Fig. 241). When the salt is added in minute quantities to water containing green pond scum, the plants (algæ) are killed.

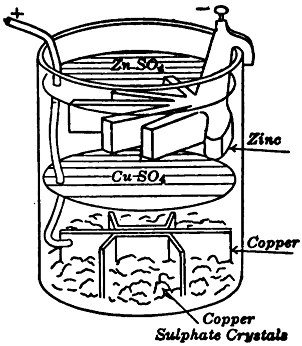

Fig. 240. Gravity cell.

449. The electric cell. We have already seen (§ 173) that when zinc dissolves in an acid the electric positive charges are transferred from the hydrogen ions to the zinc atoms:

$$Zn + 2\,H^+ \longrightarrow Zn^{++} + H_2$$

If we place a strip of *pure* zinc and another of pure copper in a beaker of dilute sulfuric acid, we have a very simple **electric cell.** It will be remembered that *pure* zinc acts but very slowly on dilute acid, and hence only a slight action will be noticed between the zinc and the acid and none at all with the copper. If, however, we connect these two strips of metal by a copper wire (Fig. 242), we shall see many bubbles of gas (hydrogen) coming from the copper. If we allow the action to continue for some time, we shall find that the zinc strip has visibly diminished and that the solution contains zinc ions. The copper is not changed, but considerable hydrogen has been liberated. If we connect a sensitive voltmeter between

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Fig. 241. Spraying potato vines with Bordeaux mixture.

the two strips, we find that a current is flowing from the copper (positive plate) through the wire to the zinc (negative plate). The ions of the electrolyte carry the electric current inside the cell from the zinc to the copper. Thus the chemical action between the zinc and the acid has been utilized to generate an electric current. ***Any electric cell is a device for converting chemical energy directly into electrical energy.***

When any two metals in the replacement series are placed in a suitable electrolyte, they constitute a cell in which the metal higher in the series is the negative pole and the lower one the positive. The farther apart any two metals stand in the series, the greater is the voltage produced by those two metals when used in a cell. For this reason the replacement series is sometimes called the **electromotive series.**

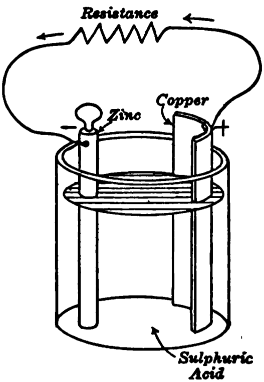


Fig. 242. Simple electric cell.

We have already seen (§ 32) that the action of acid on zinc in a hydrogen generator is greatly hastened by adding copper sulfate. The reason for this is, that a little copper is deposited on the zinc, which sets up a number of *small local electric cells.* For the same reason impure zinc dissolves rapidly in acids.

450. Electrons in the electric cell. When the zinc forms zinc ions, each atom of zinc loses two electrons:

$$Zn - 2\,e \longrightarrow Zn^{++}$$

These electrons have flowed through the copper wire from the zinc into the copper strip and have there supplied the necessary electrons to convert hydrogen ions into hydrogen atoms and molecules:

$$2\,H^{+} + 2\,e \longrightarrow 2\,H \longrightarrow H_2$$

In this way by making a complete circuit through which the electrons may travel and meet the hydrogen ion at another point in the solution, we have made zinc go into solution faster than it otherwise would. It must always be kept in mind that the flow of an electric current (as the term is used by electrical engineers) is in just the opposite direction to that of the electrons.

MERCURY

451. Occurrence and metallurgy. The principal ore of mercury is the sulfide (HgS), which is called **cinnabar**. The chief mines are in Spain and California.

Since mercury is volatile and not readily oxidized, it is easy to obtain the metal. The crushed ore is mixed with a little carbon and roasted in a current of air. The sulfur burns to sulfur dioxide, and the mercury vaporizes and is condensed:

$$HgS + O_2 \longrightarrow Hg\uparrow + SO_2\uparrow$$

The metal is redistilled to purify it.

452. Properties and uses. Mercury, or quicksilver, is a silver-white *liquid* which is 13.6 times as heavy as water.

We may pour some mercury into a glass tumbler and place an iron ball in the liquid. The iron (sp. gr. 7.9) floats.

It freezes at about −39° C. and boils at 357° C. It forms alloys (called **amalgams**) with nearly all metals except iron and platinum.

On account of its high specific gravity the metal is used to fill barometers, and because it expands uniformly it is put into thermometers.

COMPOUNDS OF MERCURY

453. Mercurous chloride, or calomel ($HgCl$). This is one of the three insoluble chlorides and therefore can be precipitated by adding a soluble chloride to a solution of mercurous nitrate:

$$NaCl + HgNO_3 \longrightarrow HgCl\downarrow + NaNO_3$$

It is a white solid which is commonly used in medicine to stimulate all organs producing secretions.

454. Mercuric chloride, or corrosive sublimate ($HgCl_2$). Mercuric chloride is a white solid, soluble in water; it is a violent poison. It is made commercially by heating a mixture of common salt and mercuric sulfate. The sulfate is prepared by the action of concentrated sulfuric acid upon mercury. A very dilute solution of mercuric chloride, sometimes called the **bichloride of mercury**, is used as an antiseptic for sterilizing surgical instruments.

SILVER

455. Metallurgy. Silver is very largely obtained through the **desilverization of lead** by **Parke's process.** Molten lead is treated with a small amount of zinc, whereupon an alloy of zinc and silver rises to the top and is skimmed off. This alloy also contains any gold which may be present. By heating it in a retort the zinc, which is a volatile metal, can be distilled off. The residue, containing lead, silver, and gold, is heated on a shallow dish in an open furnace. The lead is oxidized to the oxide, which melts and flows away, leaving a molten button of silver and gold behind.

The silver is separated from the gold by dissolving the button in hot concentrated nitric acid. The silver goes into solution as silver nitrate, and the gold is unchanged. Metallic silver is thrown out from such a solution by plates of copper which are hung in it:

$$2\,AgNO_3 + Cu \longrightarrow Cu(NO_3)_2 + 2\,Ag\downarrow$$

The metallic copper goes into solution, replacing the silver.

456. Uses. Silver is primarily used in the making of coinage, jewelry, and ornaments, and in the plating of tableware. For coinage it is alloyed with about ten per cent of copper in order to make it more resistant to the wear and tear of common use. British coins contain 92.5 per cent silver; this is an alloy known as **sterling silver.**

457. Cleaning silver. Silverware tarnishes owing to the formation of a black layer of silver sulfide (§ 188). This is usually removed by polishing with some slightly abrasive material. A recent method consists in boiling the silverware in an aluminum vessel containing a solution of sodium carbonate. The metallic aluminum in contact with the silver and the solution forms the negative pole of an electric cell; the silver serves as the positive pole. Aluminum goes into solution at the negative pole and hydrogen is formed at the positive pole. This hydrogen reduces the silver sulfide to metallic silver. In this way all the silver sulfide is gradually converted into metallic silver, which is deposited on the original ware. The equations are:

$$\mathrm{Al} - 3\,e \longrightarrow \mathrm{Al^{+++}}$$
$$2\,\mathrm{H^+} + 2\,e \longrightarrow 2\,[\mathrm{H}]$$
$$2\,[\mathrm{H}] + \mathrm{Ag_2S} \longrightarrow 2\,\mathrm{Ag} + \mathrm{H_2S}$$

COMPOUNDS OF SILVER

458. Silver nitrate ($AgNO_3$). This compound is readily prepared by dissolving silver in nitric acid and evaporating the solution:

$$3\,\mathrm{Ag} + 4\,\mathrm{HNO_3} \longrightarrow 3\,\mathrm{AgNO_3} + \mathrm{NO}\uparrow + 2\,\mathrm{H_2O}$$

It melts easily without decomposition and may be cast into sticks (**lunar caustic**), which are sometimes used in surgery to burn away abnormal growths. It is the main source of other silver compounds.

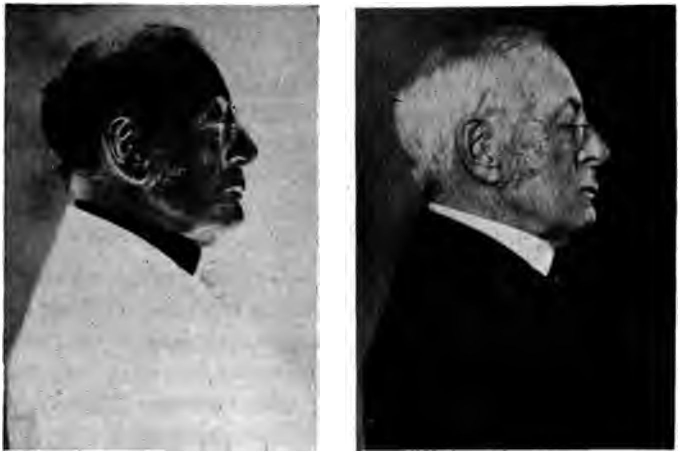
459. Silver halides. We have already learned that when a soluble chloride is added to a solution of a silver salt, a white, curdy precipitate, **silver chloride** ($AgCl$), is formed:

$$\mathrm{AgNO_3} + \mathrm{NaCl} \longrightarrow \mathrm{AgCl}\downarrow + \mathrm{NaNO_3}$$

In a similar way we may prepare **silver bromide** ($AgBr$) and **silver iodide** (AgI). These halogen salts of silver are all remarkable on account of their *sensitiveness to light.* The white silver chloride changes to a purple color on exposure to sunlight.

460. Chemistry of photography. We shall describe the production of a photograph in two steps: *first*, the preparation of the negative and *second*, the making of the print.

The glass plate or film which we buy is coated with gelatin and precipitated silver bromide (sometimes a little silver iodide also). This prepared plate is placed in a camera and **exposed** to the image which is produced by a lens properly focused on the object to be photographed. If the plate is now examined no visible effect seems to have been produced. But we can show by a further step, called **developing**, that the reduction of the silver bromide has been started on the exposed plate in exact proportion to the intensity of the light that fell upon each part.



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A *B*

Fig. 243. Negative (*A*) and Positive (*B*) of a picture of Dr. Charles W. Eliot.

To develop the latent image the exposed plate is put in a developer solution which contains a reducing agent such as pyrogallic acid or hydroquinone. The developer acts much more rapidly upon those portions of the plate where the illumination was most intense. The reduced silver is deposited in the form of a black film. Thus the plate becomes darkest where the object was brightest, and vice versa; for this reason it is called a **negative** (Fig. 243 A). The unchanged silver bromide is now removed from the plate by putting it into a solution of sodium thiosulfate (hypo). This is called **fixing** the negative. It is finally washed and dried. The whole process which we have described must be carried on in a dark room or in a light-tight box and must be carefully timed.

In **printing**, a sensitive paper is used which is coated with compounds that are very similar to those used on photographic plates. The negative is laid on the paper and the latter is so exposed that the light must pass *through* the negative. In this way the light and dark are again reversed so that we once more get a positive (Fig. 243 B). The print is developed and fixed in the same manner as the plate. The print may be *toned* by dipping it into a solution of the salts of gold or platinum. The silver goes into solution, replacing these metals, and the gold or platinum takes its place. The gold gives to the photograph a reddish brown tone, while the platinum gives it a steel-gray tone.

461. Groups of metals for analysis. We have seen that the various metals form different insoluble compounds. For example, silver, lead, and mercurous salts form insoluble chlorides. A system of **qualitative analysis** of the metals depends on the insolubility of certain salts. We can separate the metals into groups by the addition of reagents which will precipitate a salt of all the metals of a particular group. This is very convenient when we are analyzing a solution which may contain any one or all of the common metals. After we have separated the constituents of the solution into different groups, we then apply more special and complicated methods for detecting the presence in the group of any particular metal.

SUMMARY OF CHAPTER XXXIV

COPPER occurs as native copper, as the oxide, as the basic carbonate, and as sulfides. The oxide and carbonate are reduced with coal, but the sulfides require a difficult and complicated treatment.

LOW-GRADE COPPER ORES are now worked by the froth flotation process, in which the copper particles are floated away from the rock material by means of an oily foam.

ELECTROLYTIC COPPER is prepared by electrolysis, in which the anode is the impure copper plate, the electrolyte is copper sulfate solution, and the pure copper is deposited on the cathode.

USES OF COPPER — electric conductors, roofing for buildings, covering for ships' bottoms, and as one component in many alloys, such as brass and bronze.

COPPER SULFATE is the most important copper compound. It is used as a fungicide, for plating, and in some electric cells. *Cuprous* oxide is formed in testing for glucose with Fehling's solution.

AN ELECTRIC CELL is a device for converting chemical energy into electrical energy. Any two metals in a suitable electrolyte will constitute an electric cell, in which the metal higher in the series is the negative, and the lower one the positive pole.

The *rapid action* of dilute acids on *impure metals* is due to local cells which are set up by the impurities.

MERCURY is obtained from the sulfide merely by roasting. It is a heavy liquid used in barometers and thermometers.

CALOMEL, mercurous chloride, is used in medicine. *Corrosive sublimate*, bichloride of mercury, is a deadly poison and is used in very dilute solutions as an antiseptic.

SILVER is largely obtained through the desilverization of lead by Parke's process. It is alloyed with copper for most purposes.

SILVER NITRATE is made by dissolving silver in nitric acid. It is used to make other silver compounds. The *silver halides* are insoluble compounds which are sensitive to light.

PHOTOGRAPHIC PLATES are coated with silver bromide, which after exposure to light can be reduced by a developer. The unreduced silver salt is dissolved by sodium thiosulfate. Prints are made on paper coated with silver halides.

ALL METALS MAY BE SEPARATED INTO GROUPS by taking advantage of the insolubility of certain compounds. This separation of the metals into groups by the addition of different reagents is the foundation of a system of *qualitative analysis.*

QUESTIONS AND PROBLEMS

1. Write the formulas for the following ores: *copper pyrite*, *malachite*, and *cinnabar*.

2. Why is it difficult to extract copper from sulfide ores?

3. What is the principle involved in the *froth flotation process?*

4. What is meant by "electrolytic copper"?

5. Compute the weight of water in 1 kilogram of blue vitriol.

6. Write the equation for the change which takes place when a strip of iron is placed in a solution of copper sulfate.

7. How much copper goes into solution in order to replace 1 gram of silver from a solution of silver nitrate?

8. Why is zinc sometimes called the *fuel* in the electric cell?

9. Why is the replacement series sometimes called the *electromotive* series?

10. To start the action of dilute acid on zinc, a piece of platinum is put in so that it touches the zinc. Explain.

11. Commercial zinc is consumed in an electric cell even when the circuit is open; that is, when the poles are not connected by a wire. Explain.

12. In order to nickel-plate a piece of iron it is first copper-plated. How would you copper-plate iron?

13. How would you prove that a given substance contained a compound of copper?

14. Why is mercury not used in the thermometers which are carried on Arctic explorations?

15. Show how the two chlorides of mercury illustrate the Law of Multiple Proportions.

16. What special precautions should be taken in regard to handling bichloride of mercury tablets?

17. What properties of silver make it useful for coinage, for jewelry, and for tableware?

18. What compound is formed when silver tarnishes?

19. How does sterling silver differ in composition and properties from pure silver?

20. A dime contains copper and silver. How could you prove the presence of each metal?

21. What is the function of " hypo " in photography?

22. What is the purpose of toning photographic prints?

23. Why must a negative be developed in a dark room with only a dim red light?

REVIEW QUESTIONS

1. (*a*) Why does pure zinc chloride dissolved in water give an acid reaction?

(*b*) What is this phenomenon called?
(*c*) What relation has it to neutralization?

2. Under what circumstances will chemical reactions run to an end? Illustrate each case with an example.

3. If 4.0 grams of copper will combine with 1.0 gram of oxygen, and 23.7 grams of silver are precipitated by 7.0 grams of copper, what will be the percentage of oxygen in silver oxide? Show each step of your calculation and reasoning.

4. Suppose that you were given a sample of a colorless, odorless liquid. Describe briefly no less than four different experiments which would help to prove whether it was water or not.

5. What weight of silver nitrate would be necessary to precipitate the chlorine in 10 grams of crystallized barium chloride, $BaCl_2 \cdot 2\,H_2O$?

TOPIC FOR FURTHER STUDY

Chemistry of photography. How is a photographic plate prepared? What change occurs during exposure? What developer is commonly used in developing tanks? Why? What precautions are necessary in fixing, washing, and drying? What is the chemistry of blue prints, silver prints, platinum prints, and the carbon process? (*Louis Derr's* Photography for Students of Physics and Chemistry ; special pamphlets issued by the manufacturers of photographic supplies, such as the *Eastman Kodak Company's* How to make Good Pictures.)

CHAPTER XXXV

SOME OF THE LESS COMMON ELEMENTS AND THEIR USES

Gold — occurrence and extraction — properties — uses. Platinum — properties — uses. Manganese — manganese dioxide — permanganates. Chromium — oxides and hydroxides— chromates and dichromates. Tungsten, molybdenum, vanadium — the rare earths.

In this chapter we shall discuss two rare elements which are of great value, gold and platinum. We shall also briefly consider a number of elements which are not very common, but which have one or two important compounds or important uses.

GOLD

462. Mining and extraction. Gold is found almost entirely in the free state and is often distributed through quartz or sand. The process of extraction involves its separation from the great mass of surrounding material. This may be done in some cases by merely taking advantage of the fact that gold is much heavier than the other mineral matter about it. When it occurs in alluvial deposits the gravel may be washed in shallow pans in such a way that the sand, which is light, is carried away by the water and the heavy metal sinks to the bottom and is caught. In **placer mining** the ore is carried down a long trough in a stream of water; the gold settles to the bottom, where it is caught on cleats which are nailed to the floor of the trough. Another method of working the deposits involves crushing the *ore in stamp* mills (Fig. 244) and passing the crushed ore over copper plates coated with mercury. The mercury readily dissolves the gold, forming an amalgam. This amalgam is scraped from the copper plates and the mercury distilled away from the gold. Still another method, called the **cyanide process**, is used to extract the gold left in the tailings. Metallic gold is soluble in sodium cyanide ($NaCN$) solution in the presence of air and forms a compound, sodium aurocyanide ($NaAu(CN)_2$). The gold can be displaced from this solution by metallic zinc, or deposited by electrolysis.

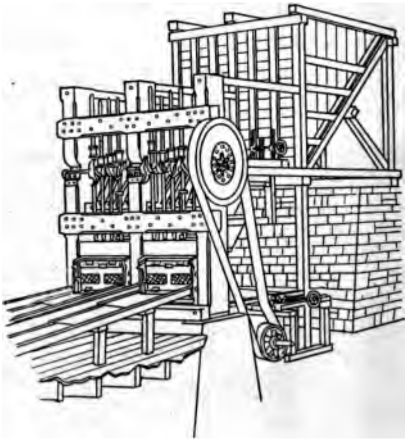

Fig. 244. Stamping mill for gold.

463. Properties. Gold is a very heavy metal (density 19.3) with a yellow color. It is the most malleable and ductile of metals and is a good conductor of electricity. It melts at about 1100° C. It is so soft that it is usually alloyed with copper in making gold coins and other gold objects. Pure gold is "24 carat" fine; gold used for jewelry is usually 18 carats.

Gold is a very inactive metal and is not affected by moisture, oxygen, or the common acids. It combines directly with the halogens and for this reason is soluble in aqua regia (hydrochloric and nitric acids mixed). **Gold chloride** ($AuCl_3$) can be prepared by the action of gold and chlorine. This substance readily dissolves in hydrochloric acid, forming **chlorauric acid** ($HAuCl_4$). This is the substance which is formed when gold is dissolved in aqua regia. The acid dissociates to give the ions H^+ and $AuCl_4^-$.

464. Uses. Gold finds its principal use as the standard of currency and exchange in almost all civilized countries. It can be beaten out into thin leaves (gold leaf) which are only $\frac{1}{250000}$ of an inch thick, and applied as a coating. The potassium salt of chlorauric acid ($KAuCl_4$) is used in toning photographs. By the use of a gold anode it can be electroplated on silver or other metals from a bath of the double cyanide of sodium and gold.

PLATINUM

Platinum is found in the free state in alluvial sands, chiefly in the streams of the Ural Mountains. Its separation from osmium and iridium, two other metals which occur with it, is a complicated process.

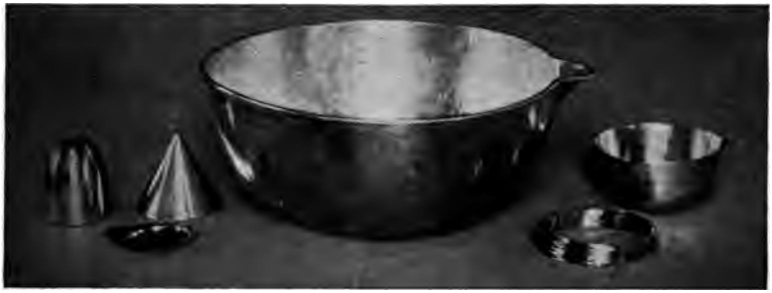

Fig. 245. Platinum dishes used in the laboratory.

465. Properties. Platinum is a whitish metal which is malleable and ductile. It melts at a fairly high temperature (1800° C.) but not in the Bunsen flame. It is affected by very few reagents but will dissolve in aqua regia, forming, like gold, a complex acid. This is called **chloroplatinic acid** (H_2PtCl_6).

When the ammonium salt of chloroplatinic acid is ignited, it leaves a porous mass of platinum known as **platinum sponge**. This sponge may be distributed over the surface of asbestos if the asbestos is dipped in chloroplatinic acid and heated. Such a material is called **platinized asbestos**. Both platinum sponge and platinized asbestos are very powerful catalysts for gaseous reactions. **Platinum black** is platinum powder made by replacing platinum from solution by means of zinc. Platinum black is also a good catalyst and is often used either dry or suspended in a liquid.

466. Uses. Since platinum melts at a very high temperature and is not attacked by most chemicals, it is a useful material in the laboratory in the form of wire and crucibles (Fig. 245). Because it has the same coefficient of expansion as glass, it was formerly the substance selected when it was necessary to seal a wire into a glass vessel. If copper wire is taken in its stead the glass invariably breaks because copper and glass contract at different rates on cooling. This use of platinum has now been superseded by **platinite** (§ 408). Since the metal is not oxidized by the air even when heated, it has been used in electrical apparatus for contact points; but now **tungsten** is taking its place, being harder and cheaper. Platinum is used in place of gold in the manufacture of rings and other jewelry. It is at present much more valuable than gold.

MANGANESE

Manganese is the only element known in Group VIIA in the periodic table. It is peculiar in that it can form many oxides. That is, it can form a number of compounds in each of which it has a different valence. In some of these it acts like a metal and forms a positive ion, and in others it is the constituent of the negative ion. Because of this multiplicity of compounds we shall not attempt to discuss the element fully.

The **manganous salts**, in which the element has the valence of two, are pink in color; they correspond somewhat to ferrous salts. The other compounds of manganese that are important are those containing oxygen.

467. Manganese dioxide. This substance occurs in nature and is known as **pyrolusite** (MnO_2). It is a strong oxidizing agent. We have already employed it in the preparation of chlorine from hydrochloric acid:

$$MnO_2 + 4\ HCl \longrightarrow MnCl_2 + 2\ H_2O + Cl_2 \uparrow$$

It will be noticed that the valence of manganese has changed from 4 to 2 in this reaction. Manganese dioxide is also used in the preparation of dry batteries, and as an oxidizing agent in black paint.

Metallic manganese and its alloy with iron (ferro-manganese) can be made from pyrolusite by reduction with aluminum (Goldschmidt process). The metal finds certain uses in the preparation of special steels.

468. Permanganates. When manganese dioxide is heated with potassium hydroxide and an oxidizing agent like potassium nitrate, a green melt is obtained. On extracting this with water we obtain a solution of **potassium manganate** (K_2MnO_4). The green solution on being diluted with water changes to a purple color, and manganese dioxide is precipitated. By evaporating the purple-red liquid we obtain needle-shaped crystals of **potassium permanganate** ($KMnO_4$). This salt in solution gives the ions K^+ and MnO_4^-. It is a very strong oxidizing agent, readily giving up oxygen to other materials and forming manganese dioxide or a manganous salt. It is used in the laboratory as an active oxidizing agent and in medicinal work as an antiseptic and disinfectant.

CHROMIUM

Chromium is a metal occurring in Group VIA. Like manganese it forms salts in which it has a number of different valences. In its higher valence it is a constituent of the negative ion of oxidizing acids.

469. Oxides and hydroxides. There are two important oxides of chromium, the green oxide, **chromic oxide** (Cr_2O_3), and the red oxide, **chromic anhydride** (CrO_3). The former is *the anhydride* of a base, chromium hydroxide ($Cr(OH)_3$).

From this base can be prepared various salts known as **chromic salts**, of which the sulfate ($Cr_2(SO_4)_3$) is important. Chromic hydroxide ($Cr(OH)_3$) is prepared by precipitation from the sulfate and is used as a mordant in dyeing.

Metallic chromium may be obtained from chromic oxide, which occurs naturally, by reduction with aluminum (Goldschmidt process). The metal is used in the preparation of special steels.

470. Chromates and dichromates. Chromic anhydride (CrO_3) readily dissolves in water, forming **chromic acid** (H_2CrO_4). The salts of this acid are called **chromates. Potassium chromate** (K_2CrO_4) is a yellow, crystalline solid, soluble in water. **Lead chromate** is an insoluble precipitate, which, as we have already seen, is a yellow pigment.

Potassium dichromate ($K_2Cr_2O_7$) is formed when we evaporate a solution of potassium chromate in the presence of sulfuric acid:

$$2\ K_2CrO_4 + H_2SO_4 \longrightarrow K_2Cr_2O_7 + K_2SO_4 + H_2O$$

The dichromate differs from the chromate by only a molecule of chromic anhydride ($K_2CrO_4 \cdot CrO_3$). In water solution it again forms the chromate ions. It is used in the tanning of leather.

Chromates and dichromates are both strong oxidizing agents in acid solutions; they are reduced to chromic salts. They are employed as oxidizing agents in the laboratory and to some extent in the industries. Potassium dichromate is used in **tanning light leathers**, since in the presence of a reducing agent chromic hydroxide ($Cr(OH)_3$) is precipitated in the leather. A solution of chromic anhydride in concentrated sulfuric acid is essentially a mixture of chromic and sulfuric acids. This is often used as a **cleaning solution** in the laboratory because it will readily dissolve greases and other material.

TUNGSTEN, MOLYBDENUM, AND VANADIUM

These three elements, like chromium and manganese, form a multitude of compounds in which they have a number of different valences and have either acidic or basic properties. The chief use of the metals lies in the preparation of special steels. The pure metals themselves are rarely manufactured; but their alloys, called **ferro-alloys**, containing about 50 per cent of iron, find important uses. The place of these metals in the steel industry has already been discussed.

471. Tungsten is a white metal which is used in making high-speed steels. It has a very high melting point (about 3000° C.) and makes an excellent metal for the filaments of incandescent electric lamps. The metal can be drawn into exceedingly fine wires which are very strong. Tungsten lamps use only about one-third as much current as the old carbon-filament lamps. The metal is replacing platinum for electrical contact points in automobile vibrators.

THE RARE EARTHS

There are about 16 elements which are very closely related to one another and form a peculiar group; all are trivalent and in a general way resemble aluminum. These elements are metals. They are known as the **rare earths** and are found in **monazite sand. Thorium** is the most important constituent of monazite sand. A thin film of thorium oxide containing about one per cent of **cerium oxide** (another rare earth) constitutes the **Welsbach mantle** (§ 257). The use of cerium oxide is another example of catalysis. Without this small amount of impurity thorium oxide gives a very inferior light when heated in a gas flame. In making the mantle the tubular fabric is dipped into a solution of the nitrates. After being dried, the mantle is heated, which burns the yarn and converts the nitrates into oxides.

SUMMARY OF CHAPTER XXXV

GOLD is found free and is obtained from the surrounding rock by mechanical separation, or by the amalgamation or the cyanide process. Gold is a heavy, soft, malleable metal. It is usually alloyed with copper to increase its wearing power. It is insoluble in most reagents but will dissolve in aqua regia, forming chlorauric acid.

PLATINUM occurs native, alloyed with similar metals. It is a very heavy, high-melting metal which is attacked by very few chemicals. It dissolves in aqua regia, forming chloroplatinic acid. Finely divided platinum is an excellent catalyst for gas reactions.

MANGANESE forms a number of series of compounds in which it has different valences. Manganese dioxide, pyrolusite, is found naturally. The permanganates are strong oxidizing agents.

CHROMIUM forms two oxides: Cr_2O_3, which is basic, and CrO_3, which is acidic. The former corresponds to the chromic salts, the latter to chromic acid. The chromates and dichromates are strong oxidizing agents.

TUNGSTEN, MOLYBDENUM, AND VANADIUM in the form of their iron-alloys are used in the manufacture of special steels. *Lamp filaments* are made of tungsten.

THE RARE EARTHS form a group of closely related elements occurring in monazite soil. Thorium and cerium oxides are used in *Welsbach* mantles.

QUESTIONS

1. The first metals known to have been used by the human race were gold and silver. Give the reason.

2. Write the equation for the decomposition of chloroplatinic acid by heat.

3. What precautions must be taken in the use of platinum vessels?

4. Gold coins are 90% gold and 10% copper. Express this in carats.

5. What reaction did we catalyze with manganese dioxide?

6. Write the equation for the oxidation of hydrochloric acid by potassium permanganate.

7. In what way is platinum better than gold for laboratory crucibles?

8. What properties has tungsten which fit it for use as a filament in electric lamps?

9. Which are the more stable, manganates or permanganates?

10. What is the difference in composition and properties between potassium chromate and potassium dichromate?

11. Write the equation for the oxidation of hydrochloric acid by sodium chromate.

TOPIC FOR FURTHER STUDY

Rare elements in industry. Recent developments have shown that some rare elements which were thought to be only of scientific interest have properties which make them of the greatest industrial importance. The scientific study of these substances has thus been well rewarded. What rare elements are commercially important? For what is each used? (*Duncan's* Chemistry of Commerce.)

CHAPTER XXXVI

RADIUM AND RADIOACTIVITY

The vacuum tube — radioactivity — radium — radium emanation — disintegration series — radioactivity and the periodic system — uses of radioactive elements — radium and the atomic theory.

In order to understand the peculiar and interesting properties of radium and of certain other elements, it is necessary to consider briefly some recent discoveries in physics.

472. The vacuum tube. If a glass tube containing air or some other gas is exhausted with an air pump until there is only a very small amount of gas left, it exhibits unusual properties when connected with a high-voltage electric current (Fig. 246). The electricity passing through the tube gives it a peculiar bluish light. Such an apparatus is called a **vacuum tube**. Careful investigation has shown that from the cathode (the negative electrode) a stream of negatively charged particles is traveling in straight lines at high speed. These negative particles are the **electrons**, which we have already considered (§ 177). Through experiments with the vacuum tube and similar apparatus scientists have discovered a great deal about electrons and their relation to matter. It has further been proved that from the positive electrode in the vacuum tube there is flowing a stream of positively charged particles of matter which are the atoms of the original gas in the tube. They are positively charged because they have lost one or more electrons; they are gaseous ions.

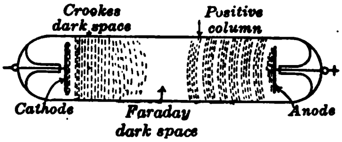

Fig. 246. Vacuum tube.

If we place a piece of metal in the path of the stream of electrons in the tube we have what is commonly called an **X-ray tube** (Fig. 247). When the electrons are stopped in their rapid flight by the piece of metal (anti-cathode), they produce a peculiar form of light energy, which passes through the glass and into the surrounding space. These are the so-called **X rays.** All light is merely a vibration, or wave motion, in the **ether,** that all-pervading material which has neither weight, volume, nor other physical or chemical properties. *X rays are vibrations in the ether which have a very short wave length* and are therefore much more penetrating than ordinary light. They are stopped by heavy metals but not by such materials as wood or paper.

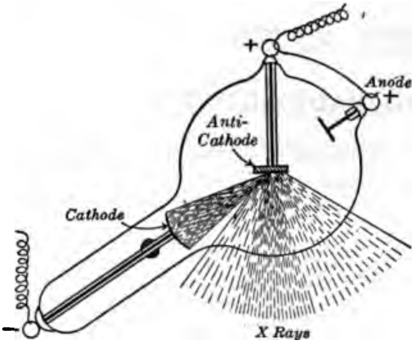

Fig. 247. X-ray tube.

The penetrating power of X rays has led to their wide use in surgery and medicine. They affect a photographic plate exactly as does ordinary light. If, therefore, we place a hand or an arm between the X-ray tube and a photographic plate, we may make a radiograph with this penetrating light. Such radiographs are especially useful in dentistry in the examination of teeth.

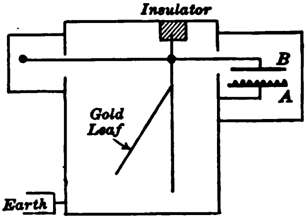

Fig. 248. Electroscope used to measure radioactivity.

The rays may be rendered visible to the eye by the aid of a **fluorescent screen.** Certain minerals (zinc sulfide) give off light when X rays come in contact with them; they are said to **fluoresce.** By holding such a mineral screen in the path of the rays, we obtain a sort of shadow picture of the object through which they have passed.

Another peculiar characteristic of X rays is their power to discharge an **electroscope**. If an electroscope is charged with static electricity (Fig. 248) the leaves will very slowly fall as the charge "leaks." If, however, the apparatus is brought near X rays it will immediately be discharged. The reason for this is that the X rays break down some of the atoms of the surrounding air into gaseous ions, and these conduct the charge away from the electroscope.

Having thus very briefly discussed certain results of physical experiments with vacuum tubes, we shall now consider some remarkable chemical elements which have attracted much attention in the last twenty years.

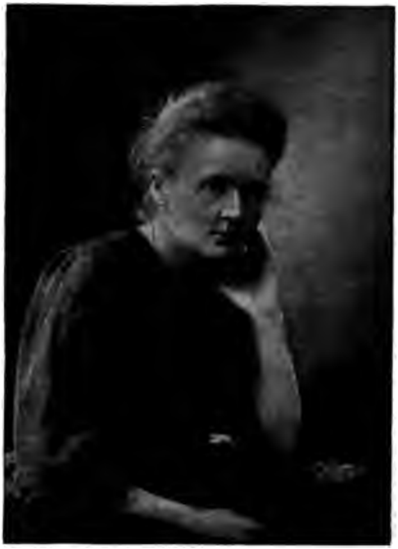

FIG. 249. MARIE SLODOWSKA CURIE (1867–).

Professor of physics at the Sorbonne, University of Paris.

473. Radioactivity. It has been found that a number of chemical elements give off peculiar radiations which have much the same effect as the X ray; that is, they will penetrate such materials as black paper, affect a photographic plate, discharge an electroscope, and cause fluorescence in certain minerals. These effects were first discovered in 1896 by Becquerel, a French scientist, as he was examining a crystal of a salt of the element **uranium**. The general phenomenon was called **radioactivity**. Pierre Curie and his wife (Fig. 249), starting with this discovery, were able to isolate two or three other elements which were much more radioactive than uranium. The first of these to be obtained was **polonium**; but radium was found in larger quantities and is the most important.

Radium is present in very minute amounts in **pitch blende** (an impure uranium oxide); only one gram of it can be obtained from every three tons of rock (Fig. 250). As might be imagined, the separation of this element involves a difficult, complicated, and laborious chemical process.

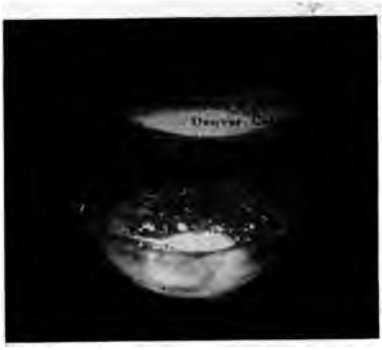

Fig. 250. Radium bromide in quartz dish.

Picture taken in dark room by means of radium rays.

474. Radium. Radium is a metal which chemically closely resembles barium and is in fact the next element below it in the periodic table. A number of its salts and the free metal itself have been prepared, and from their *purely chemical properties* there is little to distinguish the element from the rest of the calcium family.

Radium and all its salts are, however, extremely radioactive. This property is quite independent of the nature of the salts and is as apparent in radium bromide as in the free metal. In fact, what is sometimes spoken of as "radium" is in reality the salt radium bromide; it is the common form in which the element is kept and used. *Radioactivity thus seems to be a property of the radium atom* and to be independent of its chemical combination. The extreme radioactivity of radium and its salts can be shown by the effect on a photographic plate, by the discharge of an electroscope, or by a fluorescent screen.

475. Three kinds of rays from radium. It has been found that radium salts are actually giving off *three kinds of so-called* *rays*, which differ widely in their penetrating power and in the way in which they are affected by a magnetic field. The experiment shown in figure 251 illustrates the effect of the magnetic field on radium rays. Those called the **alpha** (α) **rays** have very little penetrating power and are found to be positively charged particles. The **beta** (β) **rays** are much more penetrating and are, in fact, merely a stream of electrons, exactly like those found in the vacuum tube. The **gamma** (γ) **rays** are not affected by a magnetic field and are nothing but the X rays which are produced by the action of the beta rays on some of the solid material through which they pass. It is these gamma, or X rays which give to radium the extreme radioactivity which was first noticed.

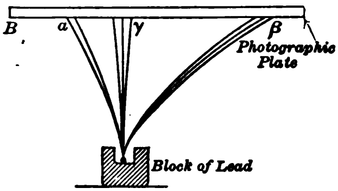

Fig. 251. Effect of a magnetic field on rays emitted by radioactive substances.

476. Energy of radium. Another very surprising property of radium and its salts is that *the nature and amount of its radioactivity are entirely independent of the temperature* and of any other known conditions. The chemist has been unable to modify in any way the radioactivity of radium. It is as strong in liquid air as it is at the highest temperature. This is very unlike usual chemical reactions, which are always greatly affected by the temperature.

There is still another remarkable property of radium salts: *they are continually producing heat* and are generally three to five degrees warmer than the surrounding atmosphere. The amount of heat evolved has been measured and found to be such that one gram of radium salt gives off 100 calories per hour. This constant evolution of heat apparently goes on indefinitely. But as a matter of fact we shall see later that this is not the case, that radium is gradually disappearing, and that at the end of 2000 years it will be half gone. Thus radium is not a source of perpetual energy, as is sometimes stated.

477. Radium emanation. We have seen that the beta rays are a stream of electrons. The *alpha rays have been shown to be positively charged helium atoms.* This very remarkable fact has repeatedly been proved by collecting enough of these "rays" to produce the characteristic spectrum of helium.

We can obtain from radium another gas which was first known as **radium emanation** but is now sometimes called **niton.** This gas is continuously being given off by radium compounds and can be pumped away from radium salts and obtained quite pure. **Niton** is clearly a definite element and finds a place in the periodic system as the last member of the family of rare gases. It is chemically inert, is monatomic, and has the molecular weight 222, exactly four units less than the atomic weight of radium. We thus see that from radium we have obtained two definite elements, one a known element, helium, and the other niton. The formation of helium and niton proceeds continuously in all radium compounds. This must be due to a disintegration of the radium atom itself; hence we have here the atom of one element actually being transformed into the atoms of two other elements. The atomic weight of niton is in this connection significant. It is exactly the difference between the atomic weights of radium and helium. *This disintegration of the radium atom the chemist cannot in any way modify or control.* He can merely observe it. Therefore, we cannot say that the chemist is able to change radium into helium and niton, but rather that the radium atom itself breaks down into these elements in spite of all that the chemist may do.

478. The disintegration series. The beta rays which are given off by a sample of radium salt are not a part of the decomposition of radium into radium emanation, but are the result of later changes. Radium emanation itself goes into another element, a solid called **radium A,** at the same time producing another alpha particle (a charged helium atom). **Radium A** disintegrates, forming successively radium B, C, D, E, and F. When radium F breaks up it forms an element, radium G, whose atomic weight is 206. In each case the change is attended by the production of an electron or an alpha particle. The electrons emitted in the later stages of the disintegration of the radium atom cause the beta rays which are given off by a sample of radium salt.

It will be noticed that the last product of the change is radium G, or **radio lead**; this is no longer radioactive because it undergoes no further changes and gives off no charged particles. This substance shows all the chemical properties of ordinary lead and cannot be distinguished from the latter except in one particular, namely, that *it has a lower atomic weight.*

Every expulsion of a helium atom in the form of an alpha particle must lower the atomic weight of the element four units (atomic weight of helium). There are five such changes between radium and radium G, the end point. Subtracting these twenty units (5×4) from the atomic weight of radium, we have 206 for the atomic weight of the final product. This is slightly lower than the atomic weight of ordinary lead, which is 207.2.

It has been noted that the lead which is found in radioactive ores (that is, ores which contain radium) has an atomic weight different from the atomic weight of the lead from ordinary ores. This lead, called radio lead (although it is *not* radioactive), was probably formed in that particular ore by the disintegration of the radium atoms. As we have said, it resembles ordinary lead *in every chemical property* and can be distinguished from it only by its *atomic weight.* In fact, if the radio lead is obtained from pure radium ore, it is found to have an atomic weight of exactly 206. These two substances must, therefore, be considered as distinct elements although they are chemically inseparable.

479. Other disintegration series. There are other disintegration series beside the radium series. Thorium seems to be the starting point of a series of radioactive elements. Radium itself has very likely been slowly formed as a product of the radioactive disintegration of uranium, and so it is probably not the starting point of a series but the middle.

480. Uses of radium. The radiations given off by radium (in particular the beta rays and their secondary product the gamma rays) are extremely active. It is possible with their aid to take pictures in exactly the same way as with the X rays generated by an electric current in a vacuum tube. Radium rays exert a very powerful action on all living matter, and it has been thought that they would be useful in curing various diseases. The results have not been so successful as was first hoped, but in treating certain kinds of cancer and similar growths radium seems to be very beneficial. Radium is extremely expensive, one gram costing about $150,000. It is, however, continually producing radium emanation, and the emanation instead of the radium itself is often used in treating diseases. Every day the emanation can be pumped off from the radium salt and collected in very tiny glass tubes. These tubes can then be inserted in the flesh near the cancer. The radium emanation in the tubes goes through the complete series of changes, ending finally as radium G and producing alpha, beta, and gamma rays. The curative power rests in the action of these rays on the diseased tissue.

Certain radioactive elements in an impure condition have been used in the manufacture of luminescent paint. They are mixed with zinc sulfide, which, as we have seen, fluoresces when in contact with radium particles.

481. Radium and the atomic theory. These astonishing facts in regard to radium appear at first sight to destroy one of the fundamental laws of science: the Conservation of Energy. The fact that radium and its compounds constantly give off heat and light without apparent loss of weight does not seem to conform to this law. But more careful experiments have *shown that* they do not give out heat and light indefinitely:

it would take about 2000 years for these compounds to lose half their activity, 2000 more to lose half of what remains, and so on. This energy of radioactive substances is apparently due to the spontaneous explosion, or disintegration, of the atoms of such elements. The emitted particles collide with each other and with the surrounding molecules, producing heat energy.

We must, therefore, modify and extend our conception of the atom as an indivisible unit of an element. The ordinary chemical reactions take place between two or more atoms; but in the case of radioactive elements we find that the changes occur *within* the atoms themselves, that the atoms are slowly disintegrating, forming other atoms and emitting electrons. According to Rutherford, who has made very extensive investigations in this field, the atom is composed of a positive nucleus surrounded by a large number of electrons. The radioactive changes are due to the breaking down of this positive nucleus, which is unstable in certain elements like radium. It is only in radioactive elements that this nucleus is unstable. The old alchemists tried to change the base metals, lead, iron, copper, etc., into gold. They believed in the possibility of the *transmutation* of one element into another. Modern chemists are quite sure that elements like iron and copper cannot be changed into gold or silver, which have a higher atomic weight; but they are equally convinced that certain elements which have very high atomic weights do form simpler atoms by disintegration. The next question seems to be how to unlock this immense quantity of energy which is stored up in atoms and how to put it to some practical use.

This new theory about atoms does not materially influence practical chemistry, since neither heat, light, nor electricity affects the rate of decomposition of radioactive elements. Yet one result has come from all of these investigations which is important for us, namely, that *there is now no question of the reality of atoms and molecules*

SUMMARY OF CHAPTER XXXVI

ELECTRONS are sent out from the cathode when an electric current passes through a highly rarefied gas. X rays are produced when electrons strike an obstacle. X rays consist of very short light waves which affect a photographic plate, cause zinc sulfide to fluoresce, and discharge an electroscope.

CERTAIN MINERALS GIVE OFF RADIATIONS LIKE X RAYS and are called radioactive. The element radium, isolated in very small amounts from an ore of uranium, is extremely radioactive.

RADIUM is chemically much like barium. Its radioactivity is independent of the chemical combination of the element. The bromide is generally used.

RADIUM GIVES OFF THREE SORTS OF "RAYS": *alpha* particles, which are charged helium atoms; *beta* rays, or *electrons;* and *gamma* rays, which are X rays produced by the *electrons.*

RADIUM EVOLVES HEAT slowly but continuously. It produces a new element called radium emanation, or *niton*, which is a rare gas. The disintegration of the radium atom into a helium atom and a niton atom goes on continuously and cannot be in any way controlled or altered. Niton also disintegrates, and there is a whole series of disintegration products from radium. The final form is radium G, or radio lead. Radio lead is chemically like ordinary lead but has a different atomic weight.

There are *other disintegration series.* Radium itself is probably formed from uranium.

RADIUM IS USED in medicine for treating cancer. Certain impure radioactive elements are used in making luminescent paints.

One result of the study of radioactive substances has been to extend greatly our atomic theory. Atoms of radioactive elements are for some reason unstable and explode, expelling either electrons or atoms of helium, or both. The atoms of most of the elements are stable and are probably made up of a positive nucleus and a number of electrons revolving about the nucleus. There is now *no doubt of* the reality of *atoms* and *molecules.*

QUESTIONS

1. How is radioactivity different from the usual chemical action?

2. Why was it formerly thought that radioactivity contradicted the Law of Conservation of Energy?

3. Why do not modern chemists try to transmute copper into gold?

4. What is meant by saying that uranium is the " parent " element and lead is the " end product " of a series of radioactive elements?

5. What important changes in our theory of atoms have been brought about by the experiments with radium?

6. Why is radium such a very costly metal?

7. What are the distinguishing properties of the alpha, beta, and gamma radiations sent off by radium?

8. How could you tell whether a substance were radioactive?

9. How could you test the activity of a radioactive substance?

10. What is the most striking difference between radium and barium?

TOPIC FOR FURTHER STUDY

Modern alchemy. The alchemists of old endeavored to transform one element into another; they failed. Today chemists can watch one element spontaneously change into another, but they can neither hasten nor retard the transmutation. How does " modern alchemy " differ from the old? (*Bird's* Science Reader, *Martin's* Modern Chemistry, and *Tilden's* Chemical Discovery.)

APPENDIX

LIST OF BOOKS FOR FURTHER STUDY

Achievements of Chemical Science — *J. C. Philip.* Macmillan and Co.

Chemical Discovery and Invention in the Twentieth Century — *Sir William A. Tilden.* E. P. Dutton and Co.

Chemistry in America — *E. F. Smith.* D. Appleton and Company.

Chemistry in the Service of Man — *Alex. Findlay.* Longmans, Green, and Co.

Chemistry of Commerce — *R. K. Duncan.* Harper & Brothers.

Chemistry of Familiar Things — *Samuel S. Sadtler.* J. B. Lippincott Company.

Creative Chemistry — *Edwin E. Slosson.* The Century Co.

Discoveries and Inventions of the Twentieth Century — *Edward Cressy.* E. P. Dutton and Co.

Essays in Historical Chemistry — *E. Thorpe.* The Macmillan Co.

History of Chemistry — *F. J. Moore.* McGraw-Hill Book Co.

Modern Chemistry and its Wonders — *G. Martin.* D. Van Nostrand Company.

Modern Science Reader — *R. M. Bird.* The Macmillan Co.

Non-Technical Chats on Iron and Steel — *L. W. Spring.* Frederick A. Stokes Company.

Outlines of Industrial Chemistry — *F. H. Thorp* and *W. K. Lewis.* The Macmillan Co.

Photography for Students of Physics and Chemistry — *Louis Derr.* The Macmillan Co.

SIX SYSTEMS OF CRYSTALS

Crystal forms. All crystals may be divided into *six classes* according to the way in which the faces are arranged about certain imaginary axes.

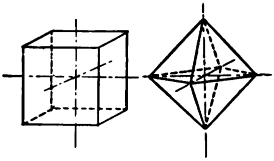

Fig. 252

I. **Isometric, or regular, system** (Fig. 252): *three equal axes at right angles to each other.* The cube and octahedron are examples. Common salt, galena, and garnet belong to this system.

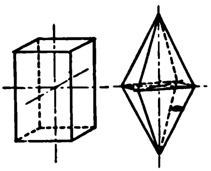

Fig. 253

II. **Tetragonal system** (Fig. 253): *two equal axes and one longer or shorter, all at right angles to each other.* Cassiterite (SnO_2) belongs to this system.

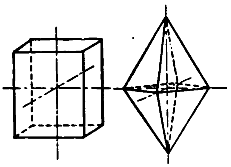

Fig. 254

III. **Orthorhombic system** (Fig. 254): *three unequal axes, all at right angles.* Sulfur, saltpeter, and magnesium sulfate belong to this system.

IV. **Monoclinic system** (Fig. 255): *two axes at right angles and a third perpendicular to one and inclined to the other.* Glauber's salt, gypsum, and ferrous sulfate belong to this system.

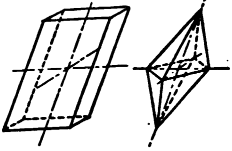

Fig. 255

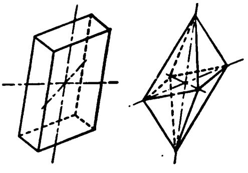

Fig. 256

V. **Triclinic system** (Fig. 256): *three axes all inclined to each other.* Crystals of copper sulfate belong to this system.

VI. **Hexagonal system** (Fig. 257): *Four axes, three equal axes in the same plane, intersecting at angles of 60°, and a fourth at right angles to all these.* Snow crystals, quartz, and sodium nitrate belong to this system. Calcite occurs in rhombic form, which is usually considered as belonging to this system.

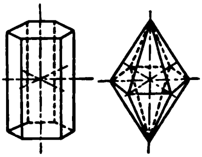

Fig. 257

For further details the reader is referred to *E. S. Dana's Minerals, and How to Study Them.* John Wiley & Sons.

SOLUBILITY OF SOLIDS IN WATER

This table shows the number of grams of anhydrous solid which when dissolved in 100 grams of water make a saturated solution at the temperature stated.

Substance	Formula	0° C.	10° C.	20° C.	100° C.
Ammonium chloride .	NH_4Cl	29.4	33.3	37.2	77.3
Barium chloride . .	$BaCl_2$	31.6	33.3	35.7	58.8
Calcium hydroxide . .	$Ca(OH)_2$	0.185	0.176	0.165	0.077
Copper sulfate . . .	$CuSO_4$	14.3	17.4	20.7	75.0
Potassium chloride . .	KCl	27.6	31.0	34.0	56.7
Potassium nitrate . .	KNO_3	13.3	20.9	32.0	246.
Sodium chloride . .	$NaCl$	35.7	35.8	36.0	39.0
Sugar	$C_{12}H_{22}O_{11}$	179.	190.	204.	487.

SOLUBILITY OF VARIOUS GASES IN WATER

(At 15° C. and under 760 mm. Pressure)

Name of Gas	Volume Absorbed by 1 Liter of Water
Very Soluble	
Ammonia	802. liters
Hydrogen chloride	458. "
Sulphur dioxide	47.3 "
Moderately Soluble	
Hydrogen sulfide	3.05 "
Chlorine	2.63 "
Carbon dioxide	1.02 "
Slightly Soluble	
Oxygen	0.034 "
Hydrogen	0.019 "
Nitrogen	0.018 "

Taken from *Kaye and Laby's* Physical and Chemical Constants. Longmans, Green, and Co.

PRESSURE OF WATER VAPOR, OR AQUEOUS TENSION

(In millimeters of mercury)

Temperature	Pressure	Temperature	Pressure	Temperature	Pressure
0° C.	4.6 mm.	11° C.	9.8 mm.	22° C.	19.8 mm.
1°	4.9	12°	10.5	23°	21.0
2°	5.3	13°	11.2	24°	22.3
3°	5.7	14°	12.0	25°	23.7
4°	6.1	15°	12.8	26°	25.1
5°	6.5	16°	13.6	27°	26.7
6°	7.0	17°	14.5	28°	28.3
7°	7.5	18°	15.5	29°	29.9
8°	8.0	19°	16.5	30°	31.7
9°	8.6	20°	17.5	50°	92.3
10°	9.2	21°	18.6	100°	760.0

DENSITIES OF IMPORTANT GASES

Approximate weight of 1 liter under standard conditions

Acetylene (C_2H_2)	1.16	grams
Air	1.29	"
Ammonia (NH_3)	0.77	"
Carbon dioxide (CO_2)	1.98	"
Carbon monoxide (CO)	1.25	"
Chlorine (Cl_2)	3.17	"
Helium (He)	0.18	"
Hydrogen (H_2)	0.09	"
Hydrogen chloride (HCl)	1.64	"
Hydrogen sulfide (H_2S)	1.54	"
Methane (CH_4)	0.72	"
Nitric oxide (NO)	1.34	"
Nitrogen (N_2)	1.25	"
Nitrous oxide (N_2O)	1.98	"
Oxygen (O_2)	1.43	"
Sulfur dioxide (SO_2)	2.93	"

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Barium					2.4
Bismuth					4.008
Boron					0.9
Bromine					6.00
Cadmium					6.7
Cæsium					1.04
Calcium					5.2
Carbon					9.10
Cerium					0.9
Chlorine					6.0
Chromium					2.9
Cobalt					5.45
Columbiu					1.7
Copper					0.4
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Germaniu					2.06
Glucinum					1.5
Gold					7.5
Helium					9.2
Holmium					4.0
Hydrogen					2.15
Indium					8.5
Iodine	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]8.7
Iridium	Ir	193.1	Titanium	Ti	48.1
Iron	Fe	55.84	Tungsten	W	184.0
Krypton	Kr	82.92	Uranium	U	238.2
Lanthanum	La	139.0	Vanadium	V	51.0
Lead	Pb	207.20	Xenon	Xe	130.2
Lithium	Li	6.94	Ytterbium		
Lutecium	Lu	175.0	(Neoytterbium)	Yb	173.5
Magnesium	Mg	24.32	Yttrium	Yt	89.33
Manganese	Mn	54.93	Zinc	Zn	65.37
Mercury	Hg	200.6	Zirconium	Zr	90.6
Molybdenum	Mo	96.0			

TABLE OF THE MORE IMPORTANT ELEMEN

with their symbols, approximate atomic weights, and val

Element	Sym-bol	Approx. At. Wt.	Valence	Element	Sym-bol	Approx At. Wt
Aluminum .	Al	27	III	Manganese	Mn	5
Barium . .	Ba	137	II	Mercury	Hg	[illegible]
Bromine .	Br	80	[illegible]	Nickel	[illegible]	[illegible]
Calcium .	Ca	40	[illegible]	[illegible]	[illegible]	[illegible]
Carbon . .	C	12	[illegible]	[illegible]	[illegible]	[illegible]
Chlorine .	Cl	35.5	[illegible]	[illegible]	[illegible]	[illegible]
Chromium .	Cr	52	[illegible]	[illegible]	[illegible]	[illegible]
Copper . .	Cu	63.6	[illegible]	[illegible]	[illegible]	[illegible]
Fluorine .	F	19	[illegible]	[illegible]	[illegible]	[illegible]
Gold . . .	Au	197	[illegible]	[illegible]	[illegible]	[illegible]
Helium . .	He	4	[illegible]	[illegible]	[illegible]	[illegible]
Hydrogen .	H	1	[illegible]	[illegible]	[illegible]	[illegible]
Iodine . .	I	127	[illegible]	[illegible]	[illegible]	[illegible]
Iron . . .	Fe	56	[illegible]	[illegible]	[illegible]	[illegible]
Lead . . .	Pb	207	[illegible]	[illegible]	[illegible]	[illegible]
Magnesium	Mg	24	[illegible]	[illegible]	[illegible]	[illegible]

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1000 grams

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